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STARCH AND ITS DERIVATIVES

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STARCH

AND ITS DERIVATIVES

By
J. A. RADLEY

M.Sc., F.R.I.C.
Chemical Consultant

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MONOGRAPHS ON APPLIED CHEMISTRY

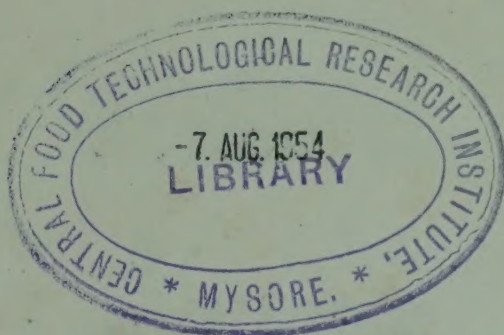
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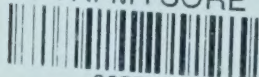
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AUTHOR'S PREFACE TO SECOND EDITION

THE need to commence an edition of this book only some eight months after the appearance on the market of the first edition is proof of the sustained interest in the subject of starch in all its various aspects. It is all the more interesting in view of the limitations of circulation due to the present state of the European and Asiatic starch-producing countries.

In this present edition of thirty-four chapters and an appendix much new material has been included, comprising some eleven entirely new or completely re-written chapters and about 1,200 new references. The chapter on Physical Chemistry has been subdivided into some five shorter chapters as, with the addition of the new material, it would have been decidedly unwieldy. The new arrangement, it is hoped, will allow of easier reference. Many new photographs and diagrams have been added better to illustrate both the previous matter and the new material.

Many new papers on starch and its uses are constantly coming forward and many of the older observations have received fresh significance and explanation. A certain amount of the old work has been discarded although in many cases the references to it remain for those who wish to follow the subject through every phase of its development. The uncertain or non-arrival of papers from Germany and the occupied countries, and the pressure of war circumstances at every stage have all contributed to the difficulties of production of this edition, but it is hoped that it includes all the more important work published to the end of 1941.

J. A. RADLEY.

AUTHOR'S PREFACE TO THIRD EDITION

THE present edition of this work was called for some nine months after the appearance of the second edition in 1943. Despite the non-availability of recent literature from Europe, the uncertain and irregular arrival of American journals and the drain imposed upon mental energy bent towards problems of 'national importance' during practically the whole of the waking hours it was decided to commence a third edition in the hope that the book would be nearly ready for press a short time after the cessation of hostilities and that too many papers would not appear from abroad to invalidate the partial labour already accomplished. Further it was anticipated that the paper position and production situation would ease to some appreciable degree with the end of the war.

Events have demonstrated the falsity of all these hopes. The last eight years have seen remarkable achievements in the elucidation of the problems of starch structure, chemistry and behaviour. These have necessitated considerable re-writing of large portions of the book if the aim of presenting a complete and up-to-date picture of the present state of our knowledge on the subject, was to be preserved. In practice this aim can only be striven for and never achieved unless the subject reaches a static condition. Post-war paper and production problems have widened the gap between the goal and its achievement since, despite all that the publishers and the author can contrive, the time between the submission of the MS. and the appearance of a book is very much wider than is desirable or than it used to be pre-war. Thus portions of a book are liable to be out-dated whilst in the page proof or binding stages.

The immensity of the subject determined the writer to extend the precedent, set in the Second Edition, of inviting the assistance of prominent workers in specialised fields of starch technology and chemistry in the task of presenting specialised sections in a concise and authoritative manner. This has led to the welcome addition of more American contributions which, it is hoped, will give a better representation of American work, practice and trends.

All the contributors have generously given me most valuable assistance, some in the face of overwork and ill health, and have felt, with me, the disappointments attendant on the various unavoidable delays that have occurred.

It is hoped, therefore, that the present edition is as up to date a review of the accumulated knowledge on the chemistry and

AUTHOR'S PREFACE TO THIRD EDITION

technology of starch and its derivatives as possible, but possibly some papers of importance from abroad may have been omitted due to their arriving too late for inclusion.

The general method of presentation used in the earlier editions received general appreciation and has, therefore, been resumed in the present edition. A number of new chapters have been added, and many of the older ones have been completely rewritten and extended by authorities in the particular fields with which the chapters deal. The chapter on the waxy cereals and starches is, it is believed, the first comprehensive account of the botany, genetics and agronomy as well as the chemistry of these materials that has appeared in print and it is hoped it will be of special interest to those whose work lies in these domains. There is also some original work included, notably in the contribution by Dr. Thomas Schoch.

As there is much of interest in the older work, providing the factual side only of this work is admitted, many of the references have been retained, generally in the form of 'Additional References'.

In the preface to the Second Edition reference was made to a number of people who helped then and it is with pleasure that the writer again acknowledges the valued help of most of them. The writer's thanks are renewed to G. V. Caesar for the additional chapter on 'Dextrinisation' and Dr. R. W. Kerr and Dr. T. J. Schoch deserve particular thanks not only for their contributions but the very personal interest they have taken in the book through all its stages. It gives me pleasure also to extend my thanks to Dr. S. Peat for his assistance which was rendered in circumstances of overwork and ill health which would have quite justified his withdrawing from the venture had he been so minded. Thanks are due, also, to Dr. J. K. N. Jones for thoroughly revising the chapter on 'The Structure of Starch from Chemical Evidence', written originally by Professor E. L. Hirst and Dr. Young for the Second Edition; to Dr. Roy Whistler; to Professor R. M. Hixon and Miss Bernadine Brimhall for their valuable contribution on the waxy cereals and starches, already mentioned above; to Professor Ed. F. Degering, who took the burden of no less than four chapters on his shoulders; to Leo M. Christensen and L. A. Underkoffler for their chapter on 'The Production of Chemicals from Starch by Fermentation Processes'; to Dr. C. W. Bice and Dr. W. F. Geddes for their authoritative contribution on the role of starch in bread staling; and last, but by no means least, to C. C. Kesler and W. G. Bechtel for their contribution on 'The Physical Methods of Characterising

AUTHOR'S PREFACE TO THIRD EDITION

Starch', which will undoubtedly be found extremely valuable by control chemicals and research workers alike. Some portions of the book appear at first sight to overlap small sections of this last contribution, but closer examination will reveal that, in these cases, the information is really complementary, so that no condensation has been made which would have tended to interrupt the development of the presentation in the few places where overlapping has apparently taken place.

A number of workers continue to send me reprints of their papers on starch and, some, letters of constructive criticism. To all of these I tender my thanks for their kindness, and hope the practice will continue.

Finally, I should like to express my appreciation of the great help and encouragement I have received from the publishers and their staff who have laboured to translate this work from pen to print, sometimes under the most frustrating circumstances.

Over the space of five years the difficulties of writing, collaborating with distant workers and producing a book covering a vast and rapidly expanding subject always introduces the possibility of omissions, errors, repetition and even minor contradictions, but in this matter the writer asks the reader for some indulgence and expresses the hope that something of merit and of value may be found in this volume. If this hope is realised then the arduous task has not been attempted in vain.

J. A. RADLEY.

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EDITORIAL PREFACE

IN these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place; and to these many will add the growth of our sense of 'values'. The value of new work in science varies greatly: the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes: he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that 'higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained'.

E HOWARD TRIPP.

AUTHOR'S PREFACE

It is hoped that this book will recommend itself to many scientific and technical workers without any lengthy apologia from the author. Like all the books that have appeared in this series, this one seeks to summarise recent progress in an important domain of chemical industry ; for starch, if not the food of the gods, is a fundamental necessity to all human beings. Though much of the text is descriptive, critical commentary has not been forgotten. The author hopes that his own experience of the industry has helped him to preserve a balance between the purely scientific and the technological, and to give just weight to diverse views on controversial points. As the manufacture of the various commercial kinds of starch has already been described at length in several useful books, this part of the subject has been treated in a broad, general way ; *per contra*, the manufacture of dextrin, about which little has appeared in print, has been treated in detail. Notwithstanding the very great amount of work already done on starch and its derivatives (as the numerous references to the literature testify), the careful reader will not fail to discern many a gap in our knowledge ; and it is hoped that he, whether he be a purely academic or a technical worker, will find in these pages some food for thought and some material upon which to base further investigations.

I have pleasure in acknowledging the help I have received from firms and individuals in compiling this volume. My thanks are due to Messrs. Imperial Chemical Industries, Ltd., for the generous permission to use their photomicrographical apparatus, and to Mr. E. Young for placing at my disposal his great micrographic skill ; to Drs. S. H. Oakshott, R. J. W. Reynolds, Messrs. H. Blackshaw, J. Faulds, P. T. Gale, N. Strafford, and J. A. Kierman for their valuable criticisms ; to the editors of various publications and to firms who have lent blocks for diagrams and apparatus ; to Prof. D. H. Cook for providing samples of tropical starches, and to other workers who have sent samples of starches or reprints of their publications. Finally, but by no means least, I thank the editor of the series and the publishers for their valuable work in converting the original manuscript into the finished book.

J. A. RADLEY.

VOLUME TWO

PART I

THE MANUFACTURE OF STARCH AND STARCH PRODUCTS

CHAPTER I

ROOT STARCHES OF COMMERCIAL IMPORTANCE

Manufacture of Potato Starch.—Potato starch is manufactured in Germany, Holland, Poland, Russia, and France (formerly also in Czechoslovakia), the inception of the industry dating from the middle of the eighteenth century. It was not until 1830 that potato starch was produced on a large scale in certain German factories. The industry became firmly established with the development of the paper and textile industries, and later when glucose was used in the fermentation industry.

A feature of the potato-starch industry is the number of small rural factories which supply the raw material, in the form of wet starch containing about 40-50 per cent. water, to factories producing glucose; the latter can thus cut down their overhead expenses by 20-30 shillings per ton, and as the crops are grown on the spot, transport costs are minimised, and the waste pulp being sold to neighbouring farms for fodder, competition with the larger town factories can be maintained.

That there is no large potato starch industry in the U.S.A. is due to the fact that development has been discouraged by economic conditions. It has not been practical for American agriculture to grow potatoes for starch. The spasmodic preparation of potato starch from surpluses and culls is an unsatisfactory foundation for a regular industry, but nevertheless some white potato starch is produced, at least intermittently, in the U.S.A. especially in Maine and Government research has encouraged a small, regular production. With the coming of waxy maize the prospects of establishing a white potato industry in America may appear to become more remote. The production of white potato starch in Maine, in 1941, was in the neighbourhood of 150 tons per day and much depends on action by the U.S. Govern-

ment whether the industry will continue to expand or not. Sweet potato starch tends to be complementary to white potato starch and not to be competitive; so that there is a possibility that the American set-up of the future will be the production of maize starch, waxy starches, sweet potato starch and white potato starch in different zones of the country most suited to the production of the raw material for each type. Maine and Aroostook County, in particular, appear to be the centre of the white potato starch industry due to the high potato yield obtainable in this area and the presence of an established industry in this area.

Both the amount and the quality of starch present in potatoes are subject to wide variations; climate, soil conditions and variety of potato playing a large part in determining these values. According to L. Raab,¹ who examined 61 varieties of potatoes, the amount of starch varies from 10-30 per cent., a normal crop yielding anything from 16-22 per cent., one yielding about 13 per cent. being regarded as poor. In America the potatoes grown in Aroostook County contain 12 per cent. of starch, but this is offset by the high yield of potatoes per acre. In Germany, by means of cross-fertilisation and careful selection, potatoes have been improved from the point of view of starch manufacture, and the average starch-content has been raised to 25-40 per cent.

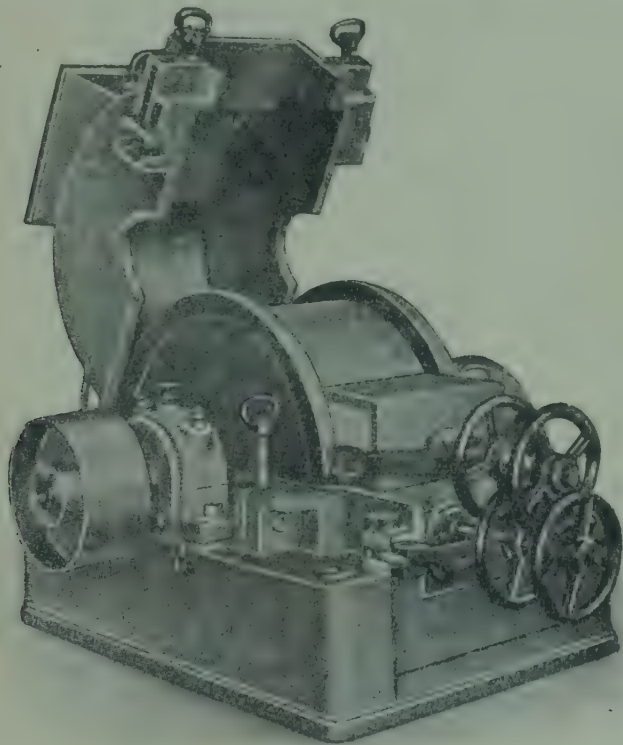
Thus in some countries potatoes are grown to supply the starch factories but in the U.S.A., where potato starch is but a small percentage of the total starch made, this is not economical. Here small, broken, misshapen or otherwise unmarketable potatoes (*culls*) or frost-damaged potatoes are used. Marketable grades of potatoes are used during glut seasons when ordinary marketing brings unfavourably ruling prices. The potatoes used in the U.S.A. contain from 14-17 per cent. starch of which 10-12 per cent., on the weight of the potatoes, is recovered. Higher yields are obtained in some very modern plants, a 95 per cent. recovery of the available starch being achieved.³⁹

Potatoes, especially those raised on heavy soil, invariably have dirt adhering to them so tenaciously that simple washing does not remove it. They are therefore soaked for several hours and then tumbled into a revolving cylinder of heavy wire which is partly immersed in a trough of running water, or they are agitated in concrete troughs. It is most important that all dirt and impurities be thoroughly removed at this point, in order that the best possible product may be obtained at the final stage.

One type of washer is a concrete trough-like affair having four washing compartments with semi-cylindrical perforated metal false bottoms in each compartment, equipped with a horizontal

shaft carrying paddles for agitating the potatoes, carrying them towards the discharge and lifting them from one compartment to the next. The washing compartments are supplied with a continuous flow of water which overflows to an under-floor drain. Between each of the washing compartments is a draining chamber.

After washing, the potatoes are thoroughly rasped or mashed in such a way as to rupture the maximum number of cells containing the starch, in order to obtain the highest yield. In one



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FIG. 1:1.—Potato rasping machine.

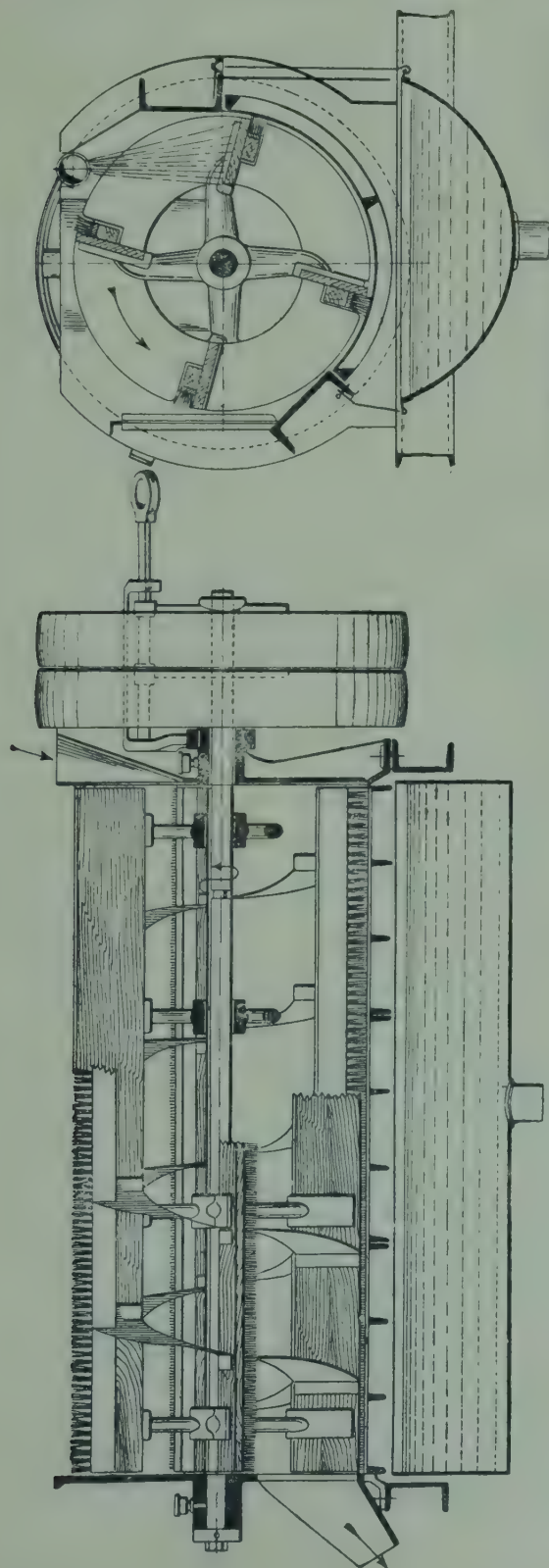
machine for this purpose a toothed cylinder revolves in an outer casing at a very high speed, generally of the order of 3,500 r.p.m. (Fig. 1:1). The resulting watery pulp is washed practically free from loose starch, and the washed pulp is passed for a further mashing to a mill, generally of the Excelsior type, in which the product passes between two discs, one of which is rotated while the other is stationary. Heavy milling by means of rollers or Buhr stones, besides costing more, tends to loss of starch by the rupture of the larger granules.

In one process,² after the raw material has been pulped, air is excluded until it is centrifuged. In the liquor discharged from

the centrifugal machine is the enzyme tyrosinase, which converts the tyrosine present into the dark bluish-black compound, melanine. In the usual processes, however, sulphurous acid is added to the pulped mass to prevent the oxidation of the tyrosine, to decolorise any melanine already formed and to prevent bacterial action besides assisting, in some manner, the separation of the starch. This is done by introducing sulphur dioxide into the pulp tank in the proportion of $\frac{1}{2}$ lb. per ton of starch present. Tyrosine can also be troublesome in giving a dark blue compound with iron in the process waters which it is, therefore, desirable to have free from iron.

The next process is washing the pulp free from starch, which is carried out on a shaking sieve. The first sieve is generally a coarse one, and a considerable amount of finely divided fibre passes through with the starch. Further passage through finer sieves (about 200 mesh) removes much of this fibre. Shaking sieves are noisy when running, are more expensive to run than those of the brush type, are apt to become clogged, and, although not so well adapted to remove starch completely from the pulp, are useful as refining sieves. They can be used to extract the first run of starch from the mash before it is returned to the mill to be remashed. In the case of brush sieves, which may be rectangular, circular or cylindrical, the brushes are moved so as to obtain the maximum sweeping effect, and to cause the pulp to travel slowly towards the discharge-outlet. Water is supplied continuously to the mass by means of overhead sprinklers when open sieves are used, and for cylindrical sieves water is sometimes emitted through jets in the central shaft itself (Fig. 1:2). The brushing movement is responsible for a large amount of fibre being forced through the mesh, which does not happen to such an extent with other sieves. Some plants use brushing sieves in the preliminary separation, a 50 mesh perforated metal sieve being first employed and the material discharging on to an 80 mesh bronze wire shaking sieve followed by a further sieve of 100 mesh.

The raw milk-starch from the sieves contains soluble matter, fibre, and a little nitrogenous matter in addition to the starch. As previously mentioned to obtain starch of a good colour the iron-content of the water used should be low,⁸ and the starch should be separated from the wash water as soon as possible, which is done by tabling the starch, whereby a lot of fibre is carried off in the liquid leaving the tables. River water may be used for washing the potatoes, and, if the design of the plant requires it, for transporting the potatoes from storage. This may be done by shovelling the tubers into water flowing in floor-level flumes

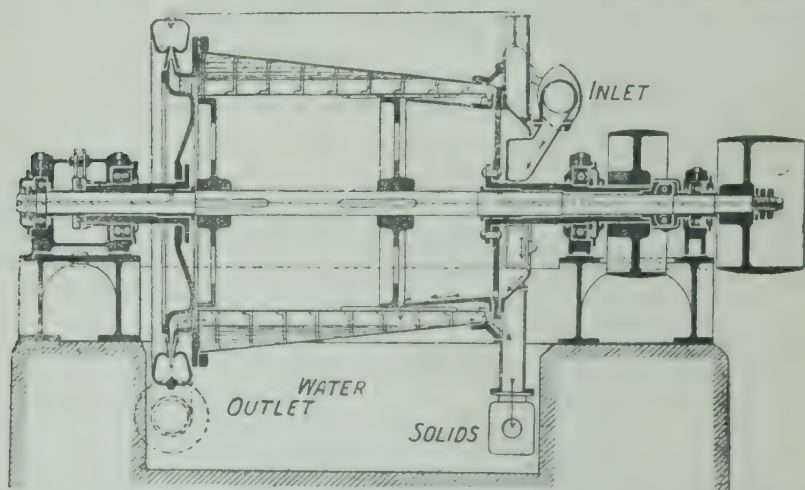


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FIG. 1:2.—Brushing sieve.

which floats them into the potato washer. Apart from these two processes, however, iron-free water should be used to obtain the best product. In some factories the liquid is removed by a centrifugal method, the liquid either passing out through the perforated circumference of the drum, which is lined with filter cloth, or if the periphery of the drum is not perforated, it is drawn off by an axial discharge-pipe. The starch is deposited against the outer wall as a compact mass, and when it half fills the drum the centrifuge is stopped and the starch removed.

Fig. 1:3 shows the cross-section of a continuous separator used in a German starch factory. The starch-milk of S.G. 1.020 enters the rotating chamber at the narrow end, the separated



[Reproduced by courtesy of 'Industrial Chemist'.]
FIG. 1:3.—Cross-section of a starch separator.

water runs to the wide end, whereas the starch is deposited on the walls of the narrow chamber and moves slowly but continuously to the narrow end, impelled by an endless screw rotating against the wall of the chamber at a slightly different rate. The discharged starch is in the form of a paste containing about 55 per cent. of moisture. Some factories use a centrifuge as a preliminary separator, the wet starch being reslurried and tabled.

When the tabling method is employed, the starch-milk is diluted and flows over inclined tables, some 20-30 yards long, about $1\frac{1}{2}$ yards wide, and 10-13 inches deep, which have a weir at the lower end. Most of the largest granules fall to the bottom in the first 8 or 10 yards, the granule-size of the starch deposited becoming progressively smaller as the weir is approached. The liquor leaving the tables carries with it, besides much fibre in suspension, some starch of very small granule-size and soluble salts. The discharged liquor is led to a battery of settlement

tanks arranged in series, where the remainder of the starch, contaminated with fibre, is deposited.

After the first sedimentation, the starch on the tables is again mixed with water and subjected to a second tabling, which may be preceded by sieving through shaking sieves to remove fibre. At this stage the starch liquor may be fed **into** centrifuges of the type in which the water escapes through perforations around the outside of the drum. In this way a starch with a lower moisture-content (35-40 per cent.) is obtained than by tabling alone (45-50 per cent. moisture). By using centrifuges after tabling, difficulties that can arise through excessive foaming of the liquor do not occur, as they do when raw starch is centrifuged in this type of machine without previous tabling.

Refining the Starch.—Refining is carried out by further washing and tabling; the wooden tables are arranged in parallel from a common supply channel and are narrower than those mentioned above. The fall of the tables is smaller, in order to reduce the rate of flow of the starch-milk. In some factories it is customary to treat the starch prior to this tabling with potassium permanganate solution in order to oxidise any impurities present, and to follow this with a sulphurous-acid treatment, but care must be taken to prevent excessive action, otherwise the starch may be so changed as to give a product which, on solution, possesses a reduced viscosity.

E. Wieg¹³ has studied the use of sulphurous acid in the manufacture of potato starch, and finds that the velocity of sedimentation of the starch from starch-milk increases with increase in the acidity of the milk above the normal. At normal *pH* the volume of the sediment gradually increases with time to the final value. With acidities greater than normal, however, the volume of the sediment rises rapidly to a value greater than the final value, and then gradually diminishes until the final value is obtained.

After the supernatant liquid has been run off, the starch on the refining tables is coated on the surface with a coloured layer containing impurities, which is scraped off with wooden squeegees and flushed away with clean water, the liquid from the flushing being returned to a starch-liquor undergoing one of the earlier steps of the process. The starch from the tables may be centrifuged to lower the moisture-content, and if washed into the centrifuge the residual impurities form the inside layer of a centrifuge cake. This inside layer is scraped off, the starch removed from the centrifuge and conveyed to the dryer.

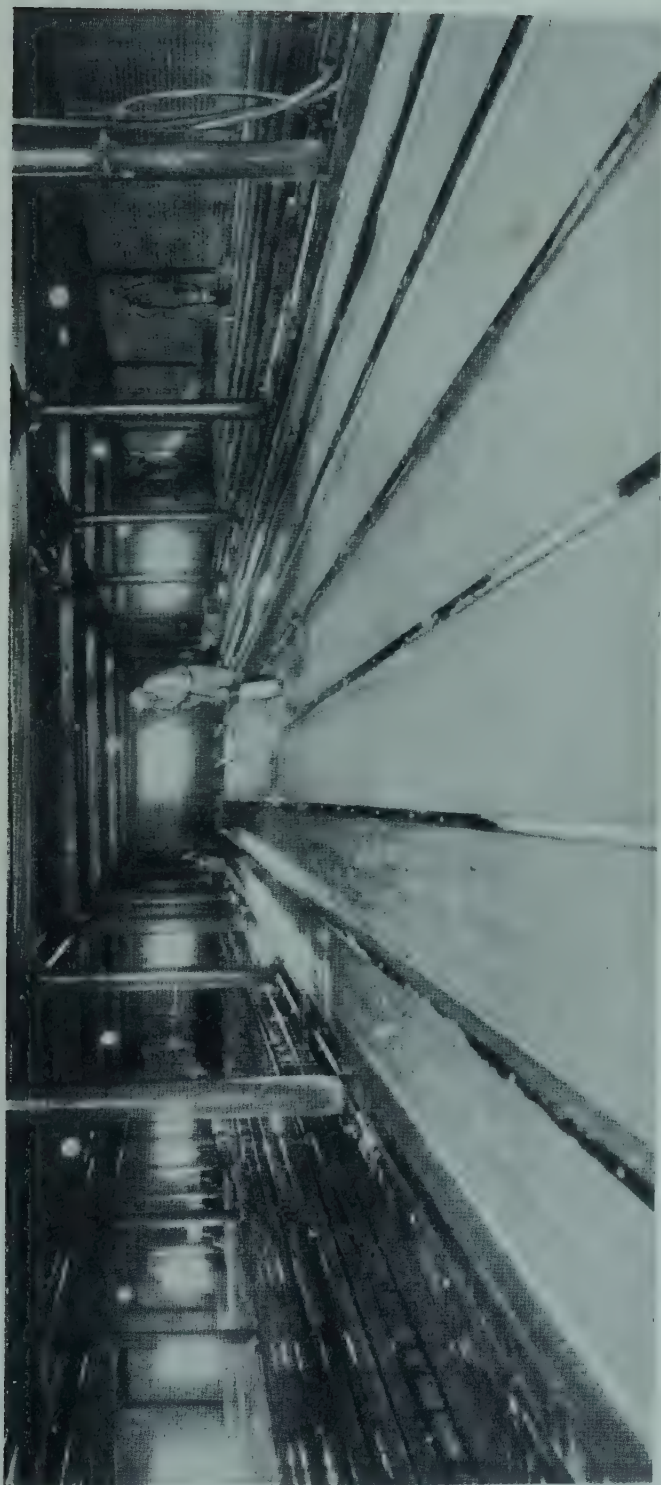
Drying the Starch.—Starch is generally dried in heated-air chambers of various designs, worked on the countercurrent

principle to avoid the formation of pellets of gelatinised starch. In one process the starch containing 35-40 per cent. of moisture enters the chamber and meets a current of air at a temperature of about 30° C. It is passed by means of endless belts to the bottom of the chamber, where the air is about 45° C. The heat is supplied by means of steam pipes between the layers of belting. In another process the starch is laid on a coarse grid at the top of a heated chamber, where some drying takes place; it crumbles and falls on to another finer grid below, and so on until at the bottom it consists of very small dry lumps and much powder. From time to time a man with a rake moves the starch on the various grids. This process is very effective, but slow, and has the disadvantage that some time is taken for the charge to accumulate during which bacterial action may operate.

Another form of dryer which gives powdered starch is the drum-dryer, in which revolving arms keep the starch continually in motion towards the discharge-vent of the drum. The axis of the drum is slightly inclined to resist the passage of the starch, and a current of warm air passes over the starch, carrying off the moisture. As an extension to this process the drum may be of the closed, vacuum type; the drum is jacketed and hot air or steam is circulated in the jacket so that the internal temperature ranges between 35° and 40° C. Grid dryers and those of either of the drum types are less apt to give a product containing pellets of gelatinised starch, which are sometimes present in starch dried in a belt-dryer through local overheating of the wet starch on the belt near the hot pipe. After drying, the starch is powdered, bolted, and bagged.

I. D. Buromskii and A. A. Matyushenko⁴ carried out some interesting work on the preparation of potato starch by fermentation. They found that frozen or thawed potatoes stored in piles, or potatoes kept under water, may undergo a peculiar anærobic fermentation of the lactic-acid type which leaves the starch intact. They also separated and described several bacteria responsible for this fermentation.

Some Difficulties Occurring in the Manufacture of Potato Starch.—The production of starch being a seasonable occupation necessitates the storing of some of the potato crop, as the whole cannot be processed at once. Temperature-control during storage is very important, and not easily realised in practice. If the potatoes are stored at -3° C. they freeze, and on thawing rot so quickly that they have to be processed immediately. The yield of starch from stored potatoes is affected by three factors: evaporation, formation of sugar from the starch



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FIG. 1:4. Flushing starch from the concrete 'tables'.

[Facing p. 8.

by the action of enzymes, and destruction of this sugar by respiration. The enzymes and bacteria present have full play at ordinary temperatures, and the metabolism of the tubers follows its normal course whereby the starch is destroyed. Respiration can take place freely, leading to a concomitant rise in temperature which, if not counteracted, accelerates the respiration still further, and the potatoes may even sprout. Both evaporation and respiration are almost arrested at 0° C. but the enzymatic production of sugar from the starch can still take place. In practice, the best temperature for storage of potatoes is considered to be between 6° and 10° C. (see also p. 174).

The reader may have seen potatoes being stored in the countryside. Long mounds, triangular in cross-section, $1\frac{1}{2}$ to 2 yds. wide and 1 to $1\frac{1}{2}$ yds. high, lightly covered with straw and a layer of earth, may be seen at the side or in a corner of a field. These mounds are known as 'clamps,' and constitute the best method of storing potatoes until the approach of warm weather. When a severe winter is expected, the amount of straw and earth covering the clamp is increased.

Frozen or diseased potatoes give rise to difficulties in manufacture, as they become soft and disperse in the wash-water. The colloidal, non-starchy matter present in suspension appears to protect the starch and prevent satisfactory sedimentation, besides frequently carrying coloured matter, which gives a poor appearance to the final product. Sedimented starch drained on the tables retains approximately its own weight of water, whereas a mass of fine potato fibres is able to retain five to seven times its weight of water. Hence fibre not only retards the settling of the starch but increases the water-retention of the 'green' starch.

H. Ducomet and A. Girard⁵ have utilised rotten potatoes for the manufacture of starch, providing that the decomposition has not been carried too far. The potatoes awaiting treatment are kept under water, which is periodically renewed, so that further decomposition is prevented. The disposal of large amounts of wash-water used in the manufacture of starch has been dealt with by J. Haline.⁶

Sprockhoff³¹ puts the loss of potato starch, in the form of starch refuse or slime, as high as 10 to 15 per cent. The slime consists of about 50 per cent. of very minute starch granules mixed with traces of proteins, fibre, iron, bacteria, etc. This form of waste is generally experienced in plants using settling vats and is due to the action of bacteria and enzymes on the slow-settling starch granules. The protein matter present is converted to a gelatinous material which protects the granules

and delays their settling. The amount of waste may be reduced to 2 per cent. by using centrifuges instead of settling tanks and by treatment of the starch-milk in the final stages with sodium hypochlorite which destroys the protective, gelatinous, protein coating on the granules, thus accelerating separation.

Potato starch has a characteristic odour, and several methods have been suggested to destroy or lessen its intensity. Thus C. Hellfrisch⁷ treats the crude starch with chlorine, and Kerr,³⁵ after treating 100 gals. of starch slurry of 22° Bé with 1·2 lb. of chlorine and holding it at room temperature for 2-3 hours, adds an antichlor, neutralises, washes and filters. This pretreatment appears to facilitate the subsequent dextrinisation of the starch. Sulphurous acid,¹¹ ozone, sulphites,¹⁰ hypochlorites, sodium carbonate, permanganates, or caustic alkali⁹ is often employed at some stage of the process to give a better-coloured product and to assist the settling of the starch. With almost all these treatments, however, care must be taken to see that the starch itself is in no way affected. Such treatments, whilst removing the characteristic odour and taste of starch so that it is satisfactory for use in edible products, fail to assist when the starch is dextrinised, as in the production of remoistening gums used for labels, stamps and envelopes. Here the use of some agents may even lead to a dextrin with an enhanced objectionable taste, unless all traces are completely removed. Throughout the whole process of making potato starch a good-grade water, as free from iron as possible, should be used in order to get good, lustrous starch. This is especially important in the manufacture of tapioca starch, in which the presence of tannin leads to the formation of iron tannate, which cannot be removed, and gives the starch a dull grey appearance, but lime and alumina have little or no effect on the appearance of the starch.

E. Peschke and F. Tobler³³ have noted that a higher yield of better starch can be rapidly and smoothly obtained by treating the starch-bearing material with *Bacillus felsineus* or the retting preparation 'felsinozima'. The cellulosic material is digested but the starch is unattacked and is obtained in a more finely granular form than by mechanical processes. In view of the interest in biological methods of production in recent years it is surprising that this observation has received so little commercial exploitation.

Cassava Starch or Brazilian Arrowroot.—This starch is obtained from the tuberous roots of the manioc or cassava plant, which was originally a native of Central America, but is now grown in Brazil, the Dominican Republic, Nigeria, Florida,

Madagascar, and the East Indies. Java and the Netherlands Indies were major sources before the war and the cost of production, due to cheapness of labour, was low. Another important factor in the popularity of tapioca or cassava starch was the high standard, demanded by the Dutch Government, of all tapioca starch for export. The question of a user inadvertently obtaining a batch of material of poor quality, for a purpose demanding a higher quality, and being disappointed, and thus prejudiced against tapioca starch, could not arise. Two chief varieties of root are cultivated, the bitter variety, *Jatropha Manihot* or *Manihot utilissima*, and the sweet variety, *Jatropha dulcis* or *Manihot palmata*. The roots usually contain a small amount of hydrocyanic acid, which, however, disappears when they are processed for extracting the starch. The bitter variety yields more starch and contains more hydrocyanic acid than the sweet variety. The acid, formed by the action of an enzyme on a glucoside,¹² phaseolunatin, is present to the extent of 0.01-0.035 per cent. in the tubers of the bitter manioc, and the cortical layers of the sweet variety contain a like percentage. The interior portions of the latter, however, contain only 0.004-0.015 per cent. of the acid.^{13, 30} On drying in the sun the content of hydrocyanic acid falls to 0.0017 per cent. and, if oven dried, to 0.0006 per cent. Y. Nemoto³⁴ considers all trace of hydrocyanic acid is removed when the tapioca flour is used for bread-making, and has studied the hydrogen-cyanide content, at various stages, in the preparation of flour, starch, etc., from different varieties of manioc. In the process of making cassava starch the formation of hydrocyanic acid must be restrained as far as possible because when liberated it forms blue iron ferrocyanide by reaction with iron salts present in the processing waters and the starch takes on a blue colour. The best starch is prepared when soft water is used in the final purification, hard water often leaving calcium oxalate in the starch.

On the average the tubers of the manioc plant contain 50-70 per cent. of water and 20-30 per cent. of starch, but the bitter manioc may contain more starch than the sweet variety and is consequently the one cultivated for starch production.

Methods of preparation vary somewhat in different countries, but in general the pulped roots are washed on sieves, and the starch so obtained is purified by more or less well-known methods. The operations of separating and purifying the starch are very similar to those used for potato starch. There is one important difference, however, between potato and cassava tubers that has a direct bearing on efficient starch separation and the procedure

used. The cells of the cassava tubers are tougher than those in potato tubers and require a much more efficient grinding process before the majority of the cells are broken sufficiently to liberate the starch. Thus it is usual not only to have more efficient mills but to pass the pulp through the grinder at least twice. Alternatively, the pulp from the mill is passed through a pulp mill. In this machine the pulp is rubbed through a special, fine-mesh sieve. Such a machine requires a relatively large expenditure of motive power. Another important difference in the two starches which has a direct bearing on the production of best quality or superior prima grades of cassava is the shape of the large proportion of the cassava granules. The concave face of these granules tenaciously holds fine dirt deposited in the concavity. All fine dirt must, therefore, be removed from the tubers before processing since once deposited on the starch it resists all simple methods of removal. In the West Indies the roots are washed, peeled and pulped, either by hand or by a simple wheel-grater, and the pulp squeezed in coarse bags to expel the juice from which a fairly pure starch is deposited. The pulp remaining in the bags is rubbed through coarse sieves, and after drying, is known as manioc flour or farine.

In the lowlands of Java the roots are grown for about 11 to 13 months, or, for better starch, 13 to 16 months. The roots are collected, cleaned, sliced or ground into meal, and dried in the sun or in kilns immediately. The dried meal is then shipped to Europe³⁸ for starch separation. Immediate drying is necessary owing to the rapid deterioration of the undried tuber brought about by the action of enzymes produced in the root. Undried roots are, therefore, never stored or shipped in this state. A large amount of starch is, however, made on the island by washing the starch from the pulped roots in a revolving cylindrical sieve of fine brass-gauze about 5 ft. in diameter and 15 ft. long. The waste matter is discharged from the end and the starch separated into two grades in a second cylindrical sieve covered with coarse cotton-cloth. The first-grade starch is deposited in about 4 hours; the second grade, which takes longer, is then agitated with water in another vat and resettled. After drying at 42° C. it is sieved through fine silk screens and bagged. The success of the operations depends chiefly on the careful control of the rate of flow of the water in the sieves.

Considerable variation may be encountered in East Indian cassava starch produced on the spot due to the multiplicity of small native mills operating and equipped with machinery in various stages of mechanical evolution. The tubers used by

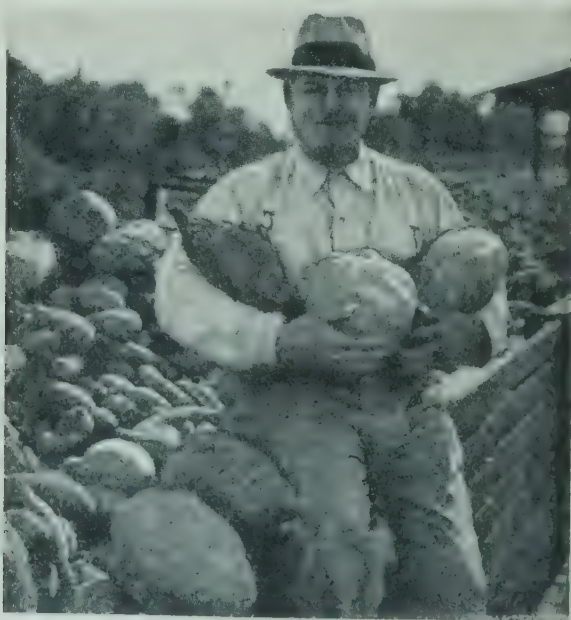
these mills may vary in variety or be a mixture of varieties of *Manihot*. Nineteenth-century Chinese methods in the Malay States included one in which the tubers were allowed to undergo a preliminary fermentation to a certain stage and then battered to a pulp which was then washed free from starch. Due to losses during fermentation and at later stages this method did not give a high total yield of starch and the material produced was of inferior quality.

When the dried roots are processed in up-to-date Javanese, European or American factories greater scientific control and better mechanical devices are employed throughout the processing so that the final starch is of fairly uniform and good quality. Alternate treatments in Jahn rasps and washing sieves serves to separate the starch from the pulp and after separation of the starch by settling it is further purified by resuspension followed by settling or centrifuging. In settling the rate of deposition is markedly affected by the nature and amount of electrolyte present and other factors being equal the anion is more effective the higher its valency.³⁵ Phosphate is quite effective, but a small addition of sulphuric acid is sometimes favoured. The final pH of cassava starch should be carefully controlled between the limits of pH 5 and 6.

Solar drying is often carried on in small Javanese factories and besides being low in cost it causes some bleaching of the final product. In modern factories, where mechanical drying is the invariable rule, centrifugal separation of the purified starch is advantageous as the wet starch cake contains some 10 per cent. less moisture than that obtained by tabling or 5 per cent. less than by filtration. Vacuum dryers, operating at 17 in. and 55° C., are used in the U.S.A. for drying the starch and have an output of 1,500 lbs. of starch of 14 per cent. moisture content per 90 minutes run with dryers 16 ft. long and 4 ft. in diameter. Other dryers include the hot-air tunnel type and the hot tunnel type in which the starch is continuously fed on to a constantly moving belt passing over steam-heated radiators in a tunnel. Such dryers are rapid in action, prevent bacterial deterioration of the starch during drying and are compact.

During the final purification of the starch sodium bisulphite may be added to the liquor to bleach the coloured impurities present. Such impurities are chiefly fine pulp particles and require a reducing bleach rather than an oxidising bleach such as is necessary to discharge the colour of the carotenoid material contaminating cereal starches. The requirements of a good grade starch are discussed in Chapter 16.

The Manufacture of Sweet-Potato Starch.—In the last few years efforts have been made in America to supply part of the domestic demand for root starches by the establishment of an industry for extracting starch from the tubers of the sweet potato (*Ipomea batata*) (see Fig. 1:5). C. H. Boehringer¹⁴ reports that this source has been used by the Japanese on a small scale for a hundred years, and that in 1933 over 30 per cent. of Japanese starch produced came from this raw material. The colour and quality of this starch is variable. The average starch-content of the sweet potato is 23·8 per cent. (maximum 26·4 per cent.,



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FIG. 1:5.—Sweet potatoes weighing 6 to 10 lb. each.

minimum 21·7 per cent.) and the final starch contains about 12 per cent. of moisture.

Experimental work in America was started as long ago as 1895 by M. B. Hardin,¹⁵ and continued for several years.¹⁶⁻¹⁸ More recent attempts by R. T. Balch and H. S. Paine,¹⁹ and by F. H. Thurber²⁰ have led to the production of a starch suitable for commercial requirements. As a very full account containing all technical details has been given by H. S. Paine and his co-workers,²¹ a brief summary here must suffice.

The potatoes are thoroughly washed, crushed in a hammer-mill (this replaces the saw-toothed drum-rasp used in European potato-starch factories), mixed with a clear saturated solution of calcium hydroxide, and the mass passed over a series of electrical

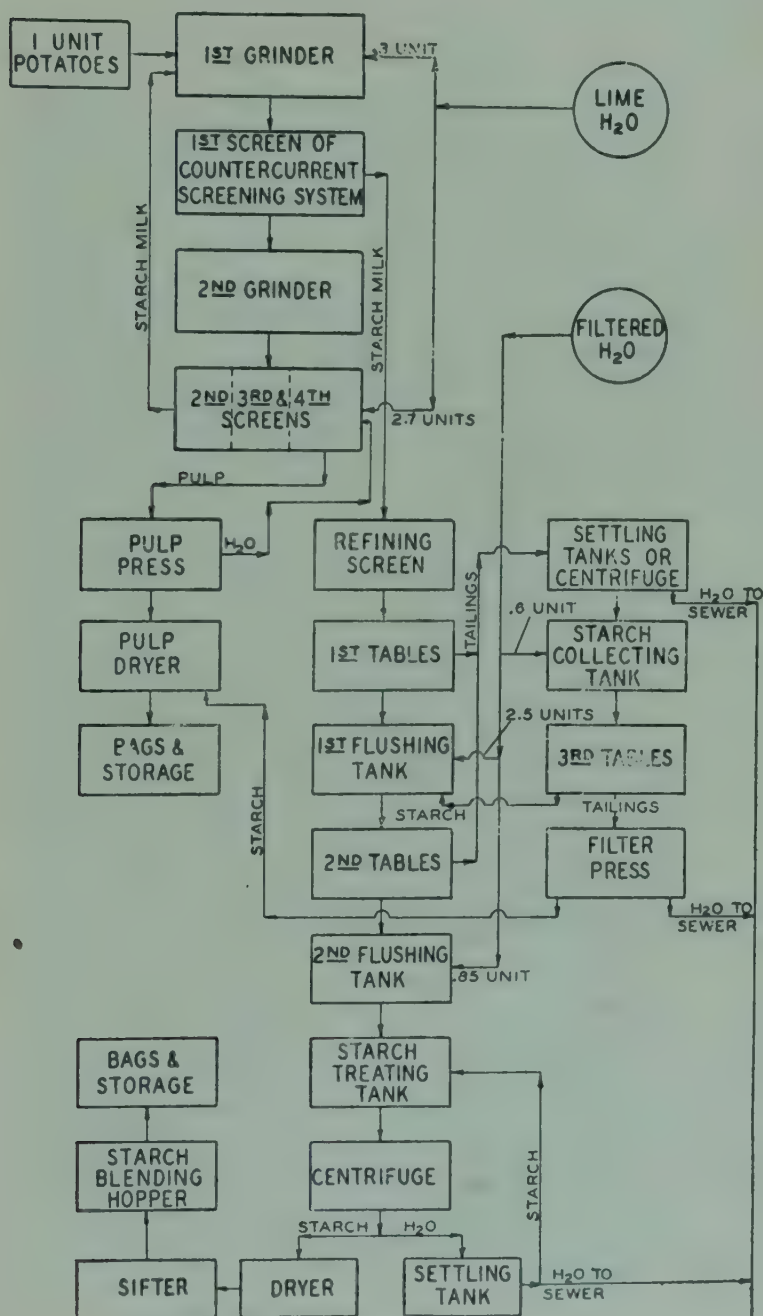


FIG. 1:6.—Flow diagram of starch process.

shaker-screens to remove the starch set free (see Fig. 1:7). The screened mash is again re-ground, washed with calcium hydroxide solution, and re-sieved, giving a suspension with a pH of 8.6-9.2, which is the optimum range for all the tabling operations; in addition, the calcium hydroxide flocculates certain impurities and dissolves the pigment present which would otherwise discolour the starch. The starch liquor is again sieved to remove fibres, etc., and tabled at about 5° Bé., the tables sloping $1/32$ -in. per ft. The tables are made of concrete, and are 19 in. wide by 110 ft. long. After sedimentation the starch is re-tabled with fresh water and the deposit from this flushed off at $10-15^{\circ}$ Bé. and re-screened. To obtain a good-coloured product, the starch from the second tabling is bleached for 2 hours with a slight excess of sodium hypochlorite at a pH value just above 8.3, the residual chlorine eliminated by the use of sulphur dioxide, and a final adjustment of pH value made. The liquor is then centrifuged in the perforate-basket type of centrifuge at 1,200 r.p.m. which delivers starch with a water-content of 35 per cent. to the dryer, which is of the batch-vacuum type, 4 ft. in diameter and 20 ft. long. After drying, the starch is pulverised and screened. Fig. 1:6 shows the flow diagram of the process.

Any starch in the overflow water from the centrifuge and in the table-tailings is recovered by cone-bottom settlers and imperforated centrifuges. It is diluted to 4.5° Bé., and after adjusting the pH value to 9.2, with saturated lime water, it is then returned to the starch going to the first tabling process, and thus the factory produces only one grade of product.

This starch has been found to be of value²² in warp sizing, and gives good, clear colours and soft 'handle' when used for finishing cotton goods. The viscosity of the starch made by the above process increases slightly during the first 3 or 4 hours of heating, which is an advantage in the above type of work (see p. 265). W. T. Scriber²³ finds that the starch gives clearness of colour, greater smoothness, and stiffness to fabrics treated in laundry work compared with other starches. It has also been found valuable for paper-making²⁴ and for the manufacture²¹ of adhesives and dextrin, where it can replace cassava starch.

Sweet potatoes do not store well, and an interesting observation made by E. F. Hopkins²⁶ is that when the sliced tubers were treated with certain vapour or liquid reagents, such as carbon tetrachloride or carbon bisulphide, the cell wall becomes very permeable to liquid, so that 60-70 per cent. of the juice present can be removed by applying pressure (see Fig. 1:8). Without this treatment only about 6-7 per cent. of the juice was removed.



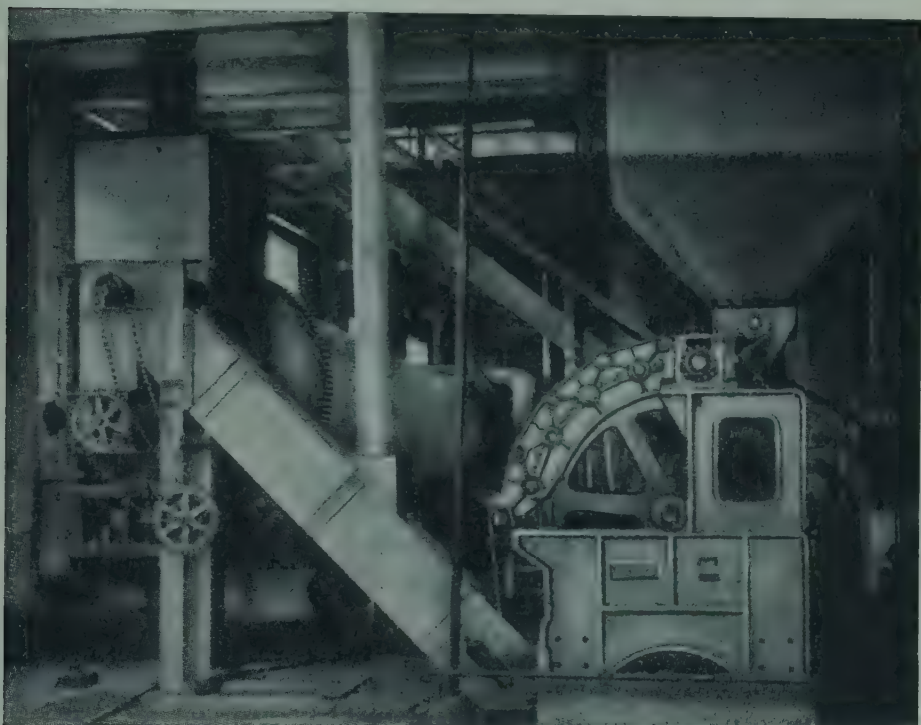
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FIG. 1:7.—A shaker screen installation.

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The remaining moisture can be reduced to 12 per cent. by using hot waste gases, and the product may then be stored until required for processing.

By finely grinding the dried material and sieving, a product is obtained having a starch-content (dry basis) of 80-90 per cent. H. S. Paine and K. Ward²⁵ find that adhesives suitable for cartons, fibre containers, etc., can be readily made from this flour, but they suffer from the drawback of possessing some colour, although for a number of purposes this is not objectionable. This flour may



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FIG. 1:8.—Pulp press and dryer.

find some outlet in the baking²⁷⁻²⁸ and brewing²⁹ industries, and it is also eminently suitable for alcohol production.

Arrowroot Starch.—This starch is obtained from the rhizomes of the tropical plant *Maranta arundinacea*, or the closely related *M. indica*; *M. nobilis* and *M. ramosissima*, native to central America but cultivated in the East and the West Indies, Australia, Natal and many other parts of the world. In the middle eighteen hundreds Bermudan arrowroot had the reputation for being the best. The root, where the aerial stem starts, is elongated, flattened and pointed. It is covered with regular scales at each section,

under these scales occur the germs by which the plant may be propagated. These scales, if not completely removed, impart a bitter taste to the starch. The active principal in the scales appears to be resinous material which, besides imparting a flavour also tinges the starch yellowish. The roots contain about 25-30 per cent. starch.

After washing, to remove the adhering soil and soften the fibrous covering, this covering is stripped off and the roots again well washed. The roots were formerly skinned with knives of German silver and pulped in roller mills, but the former operation has been discontinued and the pulping is carried out in very efficient rasping machines. As the cells of the rhizome are very tough, as are those of cassava tubers, very efficient rasping machines are required and more than one run of the pulp through the rasping machine is made. The pulp passes through the series of mills equipped with saw-like blades to tear the cells apart and hammers to convert the pulp to a paste. The liberated starch is washed from the pulp by fine water sprays and the pulping and washing processes are repeated two or more times.

The starch suspension is sieved through a series of screens of decreasing mesh size and finally allowed to settle in glazed vats. Resuspension and resettling may be carried out and the deposited starch cake is freed from discoloured surface layers, drained on trays and dried. The old method of drying was to air dry the broken starch cake on wire netting, through which it fell as it dried and crumbled, when it was collected on trays beneath the netting. More modern mills use low temperature dryers of the Thomas heater type. In these dryers the starch moves on an endless belt to regions of higher temperature progressively with decrease in water content, the final temperature being 55-60° C. Rotary dryers and vacuum dryers are also employed in some factories. By the old air drying method, drying took 3-4 days in hot weather, but under adverse conditions might take a fortnight during which souring and discolouring micro-organisms might propagate in the moist starch and spoil it. By the old method, worked in St. Vincent, J. W. Macdonald⁴⁰ claims an average recovery of 19 per cent. of starch on the weight of roots worked. By the modern methods Kerr³⁵ states that the yield is rarely more than 15 per cent. The output in the modern plant is, however, very great and one part of the old process must have contributed to a low output. This was the feature of working the fibrous pulp by hand in a current of water in a perforated box. With mechanical washers the fibrous character of the pulp is apt to cause it to collect in jumps.

REFERENCES

1. L. RAAB, *J. Chem. Soc.*, 1872, **25**, 1111.
2. JAHN & Co., E.P., 439,262, 3/12/1935.
3. E. WIEGL, *Zeit. Spiritusind.*, 1935, **58**, 205.
4. I. D. BUROMSKIĭ and A. A. MATYUSHENKO, *Microbiol., U.S.S.R.*, 1936, **5**, 40; via *Chem. Abstr.*, 1936, **38**, 11C, 6030.
5. H. DUCOMET and A. GIRARD, *Compt. rend. Acad. Agric. France*, 1917, **3**, 61.
6. J. HALINE, *J. Soc. Chem. Ind.*, 1916, **35**, 1126.
7. C. HELLFRISCH, E.P. 24,456, 1895.
8. O. SAARE, *Zeit. Spiritusind.*, 1886, **9**, 511.
9. — *ibid.*, 1892, **15**, 319, 335 and 344.
10. ANON, *ibid.*, 1918, **41**, 399.
11. — *ibid.*, 1918, **41**, 407.
12. CARMODY, *Lancet*, 1900, No. 4018, 736.
13. DUNSTAN, HENRY, and AULD, *Proc. Roy. Soc.*, 1906, **78B**, 152.
14. C. H. BOEHRINGER, *Assist. Trade Commiss. Tokyo, Spec. Rept.*, 1936, **55**, Jan. 7th.
15. M. B. HARDIN, *S. Carolina Agric. Exp. Station, Ann. Rept.*, 1895.
16. F. H. SHIVER, *ibid.*, *Bulletin.*, 1898, **28**; *ibid.*, 1901, 63.
17. C. C. McDONNELL, *ibid.*, 1908, 136.
18. T. C. KEITT, *ibid.*, 1912, 165.
19. R. T. BALCH and H. S. PAINE, *Ind. Eng. Chem.*, 1931, **23**, 1205.
20. F. H. THURBER, *ibid.*, 1933, **25**, 565 and 919.
21. H. S. PAINE, F. H. THURBER, R. T. BALCH, and W. R. RICHEL, *ibid.*, 1938, **30**, 1331.
22. F. H. THURBER, *ibid.*, 1933, **25**, 565.
23. W. T. SCREIBER, M. N. GEIB, and C. C. MOORE, *Bur. Stds., J. Res.*, 1933, **11**, 765.
24. C. G. WEBER, M. D. SHAW, and M. J. O'LEARY, *Nat. Bur. Stds. Misc. Publ., M.* 150, 1935.
25. H. S. PAINE and K. WARD, U.S.P. 2,124,994, 1935.
26. E. F. HOPKINS, *Science*, 1938, **87**, 71.
27. C. E. MANGELS and S. C. PRESCOTT, *Chem. Age (N.Y.)*, 1921, **29**, 132.
28. H. C. GORE, *Ind. Eng. Chem.*, 1923, **15**, 1238.
29. H. S. PAINE and E. YANOVSKY, U.S.P. 2,126,133, 1938.
30. C. C. MOORE, *U.S. Bur. Chem., Bull.* 106, 1907.
31. SPROCKHOFF, *Zeit. Spiritusind.*, 1930, **53**, 78.
32. R. D. DE G. PAULA and J. L. RANGEL, *Ministerio trabalko, ind. comm., Inst. nac. tec. (Rio de Janeiro)*, 1940, 66; via *Chem. Abstr.*, 1940, **34**, 7031.
33. E. PESCHKE and F. TOBLER, *Faserforsch.*, 1925, **4**, 252; *Chem. Zentr.*, 1925, **96**, II, 1233.
34. Y. NEMOTO, *Rev. Aliment. Chim. Ind.*, 1940, **4**, No. 33, 5.
35. R. W. KERR, *Chemistry and Industry of Starch*, Academic Press, N.Y. 1944.
36. *U.S. Tariff Comm. Rept.*, 138, 42, 1940.
37. R. M. HIXON and G. F. SPRAGUE, *Ind. Eng. Chem.*, 1942, **34**, 959.
38. — *Rept., Agr. Res., Part II*, Iowa Corn Res. Inst., 3rd Ann. Rept., 1938, p. 61.
39. C. A. BRAUTLECHT, *Ind. Eng. Chem.*, 1940, **32**, 893.
40. J. W. MACDONALD, *J. Soc. Chem. Ind.*, 1887, **6**, 334.

ADDITIONAL REFERENCES

- ANON., *Amer. Dyestuff Rep.*, 1936, **25**, 313; *Bull. Assoc. Chim.*, 1936, **23**, 553. (Recent equipment for separating tuber starches.)
- L. W. JIRAK, *Zeit. Spiritusind.*, 1935, **58**, 165. (Methods and calculations for plant control.)

- W. KRÖNER, *ibid.*, 1937, **60**, 39 and 45. (Black substance deposited on potato-starch machinery due to proteins.)
- H. G. KNIGHT, *Mfrs. Record*, 1937, **106**, 40. (Sweet-potato starch manufacture.)
- W. KRÖNER and G. STEINHOFF, *Zeit. Spiritusind.*, 1937, **60**, 143. (Estimation of starch in frozen potatoes.)
- W. TAEGENER, *Deut. Zuckerind.*, 1937, **62**, 69. (Estimation of starch in potatoes.)
- C. P. McCORD, *Mfg. Conf.*, 1927, 621. (Starch-drying precautions.)
- P. NETTIN, *Rev. Sci.*, **65**, 363. (Technology of starch-making.)
- J. A. MACLACHLAN, *J. S. Afric. Chem. Inst.*, **12**, 3. (Manufacture of starch.)
- M. SPROCKHOFF, *Zeit. Spiritusind.*, 1929, **52**, 306. (Sources of waste in starch manufacture.)
- A. H. CROWN, *Proc. Amer. Assoc. Text. Chem. Col.*, 1930, **59**; *Amer. Dyestuff Rep.*, 1930, **19**, 83. (Manufacture of starch, dextrin, and British gums.)
- G. J. MULLER, *Chem. Met. Eng.*, 1941, **48**, No. 3, 78 and 83. (Modern technology in potato starch manufacture.)
- G. E. GOVIER, *Rubber Age*, 1930, **10**, 490. (Manufacture of starch for the rubber industry.)
- C. H. PETERS, *Zeit. Spiritusind.*, 1930, **53**, 120. (Starch industry in Russia.)
- T. MINAGAWA, *J. Agric. Chem. Soc. Japan*, 1933, **9**, 342; via *Chem. Abst.*, **27**, 3959. (Amylosynthase and synthetic starch.)
- J. T. GIBBONS, *Amer. Dyestuff Rep.*, 1934, **23**, 286. (Manufacture.)
- H. P. DAS GUPTA and V. SUBRAHMANYAN, *Agric. Livestock, India*, 1934, **4**, 645. (Starch from indigenous tubers and grains.)
- W. D. HANSEN and H. VOGEL, *Mitt. deut. Landw. Ges.*, 1926, **41**, 12. (Potato starch.)
- MARILLER, *Bull. Assoc. chim. suc. dist.*, 1927, **44**, 299. (Purification and drying of potato starch.)
- M. SPROCKHOFF, *Zeit. Spiritusind.*, 1928, **51**, 180. (Grating machines used in potato-starch manufacture.)
- *ibid.*, 1929, **52**, 191. (Yield tables for potato starch.)
- O. WOLFF, *ibid.*, 1929, **52**, 110, 221, 231. (Control operations in potato-starch manufacture.)
- W. BUDDEBERG, *ibid.*, 1930, **53**, 113. (The 'ter Meer' centrifuge in potato-starch manufacture.)
- M. SPROCKHOFF, *ibid.*, 1930, **53**, 119. (Potato starch.)
- *Chem.-Ztg.*, 1933, **54**, 299. (Tables showing starch-content of starch-milk in relation to density.)
- W. BIELECKI, *Przemysl Chem.*, 1930, **14**, 145. (Potato starch.)
- J. EBEL, *Chem.-Ztg.*, 1933, **56**, 829. (Advances in potato-starch manufacture.)
- B. BLEYER, *Zeit. Spiritusind.*, 1933, **56**, 45. (Potato starch.)
- H. TRVLLER, *ibid.*, 1933, **56**, 60. (Effect of weather on potato starch.)
- B. HOSPEL, *ibid.*, 1935, **58**, 237. (Yield tables in potato-starch manufacture.)
- J. JIRAK, *ibid.*, 1935, **58**, 81. (Control of washing-out process in potato-starch manufacture.)
- M. PLATZMANN, *ibid.*, 1936, **59**, 361. (Starch-content of potato flakes.)
- P. A. SINGER, U.S.P. 1,528,995, 1925. (Drying moist starch in hot air cyclone separator.)
- N. E. GOLDTHWAITE, *Colorado Agric. Exp. Stat. Bull.*, 1925, (296), 3. (Composition of Colorado potatoes.)
- B. LAMPE, *Zeit. Spiritusind.*, 1931, **54**, 36. (Determination of starch-content of potatoes with Reimann balance.)
- G. FOTH, *ibid.*, 1924, **47**, 352. (Determination of starch in potatoes of very low starch-content.)
- MASCHINEBAU-ANSTALT HUMBOLDT, G.P. 441,911, 1925. (Potatoes treated in disc mills open to the whole circumference of the discs.)
- C. J. DE WOLFF, *Chem. Weekblad*, 1927, **24**, 18. (Formation of sugar in potatoes during drying.)

- W. KRÖNER, *Zeit. ges. Getreidew.*, 1939, **26**, 162. (Flow sheet and details of potato-starch manufacture with analytical details.)
- *Zeit. Spiritusind.*, 1939, **62**, 163. (Furnace gases which contain SO₂ should not be used for drying starch.)
- W. R. RICHEL, *Proc. Oklahoma Farm. Chemurgie Conf.*, 1937, **1**, 4. (Plant operation for sweet-potato manufacture discussed.)
- C. C. MOORE, *Potato Mag.*, 1920, **2**, 10, 20, 22; **3**, 8, 20, 22. (Detailed description of potato-starch manufacture.)
- W. EKHARD, *Zeit. Spiritusind.*, 1924, **47**, 183. (Potato-starch manufacture.)
- H. S. PAINE, F. H. THURBER, R. T. BALCH and W. R. RICHEL, *Chem. Met. Eng.*, 1939, **46**, 69. (Sweet-potato starch.)
- E. SZEGO, *Bull. assoc. Chim.*, 1939, **56**, 158. (Plant control in potato-starch factories discussed.)
- W. KRÖNER, *Fr.P.* 823,308, 18/1/1938. (Starch separated from finely divided potatoes by upward stream of water in inclined tube.)
- A. FRANK, *Rev. brasil. chim.* (Sao Paulo.), 1940, **10**, 120. (Preparation of cassava starch.)
- H. G. KNIGHT, *Kansas State Hort. Soc. Biennial Rept.*, 1940, **45**, 131. (Sweet-potato starch. General.)
- E. SZEGO, *Inds. agr. et aliment.*, (Paris), 1947, **64**, 71-9. (Potato-starch manufacture by modern methods.)
- F. W. ZERBAN, *Bull. assoc. chim.*, 1945, **62**, 146-8. (pH in potato-starch liquors should be maintained at approx. 4 to allow good separation of starch from protein.)
- A. H. A. DE WILLIGEN and A. J. REESTMAN, *Verslag. Landb. Onderzoek.*, 1946, **50B**, 619-53. (Investigations of starch content of industrial potato varieties.)
- W. W. HOWERTON and R. H. TREADWAY, *Ind. Eng. Chem.*, 1948, **40**, 1402-7. (Comparison of batch and continuous processes in the manufacture of white potato starch.)
- W. SECH and G. RUDORFF-FISCHER, *Vorratspflege u. Lebensmittelforsch.*, 1940, **3**, 473-80; *Chem.Zentr.*, 1941, **1**, 2191. (Alteration in starch during manufacture from potatoes discussed from dietetic and culinary viewpoints.)
- W. KRÖNER and F. WITT, *Z. Spiritusind.*, 1940, **63**, 33-34. (Filtering and centrifugal methods of separating potato pulp and juice discussed.)
- W. KRÖNER, *Z. Ver. Deut. Ing. Verfahrenstech.*, 1940, 183-189. (Potato-starch manufacture diagrammatically described with flow diagrams.)
- W. KRÖNER, *Mehl u. Brot.*, 1940, **40**, 325-9. (Production and use of potato starch and starch products.)
- A. K. R. CHAUDHURY, *J. and Proc. Inst. Chem. (India)*, 1945, **17**, 134-6. (Analytical figures for sweet potato and the separation of the starch discussed.)
- B. A. BOURNE and F. H. THURBER, *Southern Power and Ind.*, 1946, **64**, No. 6, 44-7, 98, 100. (Starch production from sweet potatoes described in detail.)
- H. G. KNIGHT, *Kansas State Hort. Soc., Biennial Rept.*, 1940, **45**, 131 5. (The production and utilisation of sweet-potato starch discussed.)
- YUKIO TOMIYASU, *Japan P.*, 129,721, 11/4/1939. (Manufacture of sweet potato starch and utilisation of the juice.)
- ANON., *Bull. Imp. Inst.*, 1934, **32**, 370. (Constitution of Brit. Honduras Cassava: *ibid.*, 1934, **32**, 374. (Constitution of *Zamia Furfuracea* starch from B.H.)
- O. RIBEIRO, *Anal. Assoc. quim. Brasil*, 1942, **1**, 264-9. (The acidity of grated manioc flour.)
- K. H. MEYER and P. HEINRICH, *Helv. Chim. Acta*, 1942, **25**, 1639-50. (Composition of starch from leaves, seeds and tubers of potato show marked difference in amylose/amylopectin ratio.)
- I. A. VESELOVSKY, *Amer. Potato J.*, 1940, **17**, 330. (Ratio of large to small grains is varietal characteristic. Significance of grain size in industrial applications and data for many varieties discussed.)
- J. H. PAYNE, G. J. LEY and G. AKAN, *Hawaii Agr. Expt. Sta. Bull.*, 1941, **86**, 3.

- (Detailed study of taro (*Colocasia esculenta*) processing, analyses and uses. Taro flour used by wheat-allergic people.)
- R. BASTIN, *Bull. agric. Congo Belge*, 1939, **30**, 258. (Chem. analyses, morphological characteristics and reactions of three exotic starches given.)
- COURS, *Agron. Trop.*, 1946, **1**, 138. (Study of variations in granule size of manioc starch with variety.)
- BLEIER, *Food Trade Rev.*, 1947, **17**, No. 5, 5. (Recovery of starch lost in dicing and peeling potatoes in food factories discussed.)
- H. E. REICHENBERG, *Chem. Engng.*, 1949, **56**, No. 6, 120. (Description of potato-starch manufacture in U.S.A.)
- A. A. THORNTON, B.P. 588,313, 8/2/1945. (Extraction of starch by centrifugal method. Photo-electric cell used to control washing process.)
- BRAUTLECHT, *Food Packer*, 1946, **27**, No. 12, 70. (Starch content of white potatoes used in starch manufacture in Maine discussed.)
- S. N. OSTANIN, *Khim. Referat Zhur.*, 1940, No. 8, 37. (Properties of starch from new kinds and various grades of potatoes.)
- H. N. BARHAM, *Agric. Exp. Sta.*, Manhattan, Kansas, 1947, 1226; *Biol. Abstracts* 21, *Kansas State Hort. Soc., Bienn. Rept.*, 1946, **48**, 84. (Discusses improvements in and uses of sweet potato-starch. Changes in starch during curing of tubers very important.)

CHAPTER 2

WHEAT, RICE AND SAGO STARCHES

The Manufacture of Wheat Starch.—In the manufacture of wheat starch the chief problem lies in the separation of the starch from gluten. Gluten consists of two protein substances, glutenin and gliadin, and in water swells to a sticky mass which retains the starch. A review of the state of our present knowledge of wheat proteins has been made by D. B. Jones,⁵ to which readers are referred for further information. A. Schhukin⁷ has examined the chemical composition of hard and soft wheats (see also Table XXV, p. 379). To separate the starch, the gluten may be destroyed by fermentation, as in the older processes, or mechanically kneaded in flowing water, by which the starch is liberated and carried away. Processes based on the mechanical separation are in general use to-day, as the gluten can be recovered and is a valuable by-product.

Wheat starch may also be readily prepared from old or damaged wheat. M. M. McMasters and G. E. Hilbert⁸ find that wheat stored for 15 years in a cool, dry, well-ventilated place is still quite suitable for starch production although starch recovery appears to decrease as the starch ages. However, the properties of the starch are not altered by ageing of the wheat.

Among the common types of damage to wheat are sourness, mustiness, weathering, frost scab and blight weevil and mould. Sprouting, incipient heating and heat do not render wheat unfit for starch production although if the heat damage is extensive, or many dead germs are present, the properties of the starch may be modified. Some types of damaged wheat may yield starch which is slightly off-colour or off-odour. Microscopically, starch from damaged wheat cannot be distinguished from that from sound wheat.

In the old fermentation method (*v.s.*), often known as Hale's method, the grain is steeped until it is soft enough to be coarsely crushed in a mill, the temperature of the steeping water playing a large part in determining the time of steeping. This preliminary steeping may, however, be omitted. A mash is made of the crushed grain and left to ferment. The period of induction of fermentation can be shortened if liquor from a previous fermenta-

tion is introduced into the mass. The period of fermentation required to bring the mass to the required state varies with climatic conditions. In the summer about 7 to 10 days are required, and in the winter the process may take as long as 30 days. Proteins and other nitrogenous matter decompose during the fermentation, and acids are produced which in turn help to dissolve the gluten, the latter becoming more soluble as its degradation proceeds. Gases, chiefly carbon dioxide, ammonia, and hydrogen sulphide, are evolved in the early stages of the process, and the whole mass has an offensive, putrefying odour, which constitutes a drawback to the process. As the fermentation proceeds, the mass becomes acid from the formation of acetic, butyric and lactic acids, and clots of moulds appear on the surface. The fermentation should not be carried to the stage at which the liquid becomes viscous, as it has then proceeded too far and difficulties will be encountered. At the desired stage, supernatant liquor is run off and the remaining sludge transferred to washing drums. The suspension of starch flows out through the wall of the drum, which may be made of cloth or fine metal-gauze. By revolving the drum horizontally and passing in water through the central shaft the mass may be washed until very little starch remains. The starch-milk is run off by means of troughs to settling tanks, where it is washed several times by agitation, settling, and decantation. The mass of starch is then removed to draining-boxes lined with flannel, or it is spread upon porous draining-floors, after which it is sent to the drying room.

The fermentation process is rarely, if ever, used at the present time. Not only is the valuable gluten lost, but the process is a lengthy one, offensive in operation, and gives rise to effluents, the disposal of which offers difficulties.

The Alsatian Process dispenses with fermentation, and is occasionally employed on the Continent. The grain is steeped until soft and the steeping water is changed frequently to avoid acid-formation and fermentation. The grain is then roughly crushed and the mass kneaded in a continuous stream of water supplied from sprinklers over the trough. The process is slow, as about 10 hours are required for the treatment of 1 ton of wheat. It has the advantage, however, that good-grade gluten is recoverable if the steeping is not too prolonged. A temperature of 30° C. is recommended by Rehwald to hasten this step of the process. One ton of wheat yields about 750-1,000 lb. of first-quality starch and about 220-450 lb. of starch of second quality.

Martin's Process is the one most generally used now, partly

owing to the low initial outlay for plant, and partly to the good yields of first-quality starch obtained. About 45-55 per cent. of good starch on the weight of wheat, 10-20 per cent. of inferior starch, and 10-15 per cent. of good-grade gluten free from husks may be obtained. The disadvantages of the process are the higher-priced starting materials and the relatively large yield of second-grade starch, contaminated with gluten, that is produced. This, however, can be utilised as a good basic material for sizes and adhesives. It is a fairly rapid process. Wheat flour, the starting material, is made into a dough with about 40 per cent. its weight of water and allowed to stand for 1 hour. The gluten swells, and the mass is transferred in lumps to the washing-machine, in which the dough is kneaded by means of a grooved roller on a grooved bed flanked by sieves, while a constant stream of water is supplied by means of sprinklers. The starch-milk is collected in troughs beneath the machine and is led into settling-tanks. The remaining gluten is removed after each operation.

Fesca's Process also uses flour as the raw material, and separates the starch from the gluten by means of a centrifuge. A suspension of flour in water is made and centrifuged, using a non-perforated drum. In this way a layer of starch is obtained on the wall of the drum, whilst the gluten forms a layer on the inside, a certain amount of gluten also remaining in suspension. Knives or scrapers, that may be set at a required distance from the centre of the centrifuge drum, are used for scraping off the gluten layer. The liquid from this process is rich in nitrogenous material and mineral salts and is incorporated in feeding-stuffs, which are then dried. To obtain a sharper separation of the starch from the gluten, Klopfer has suggested several modifications of this process, namely, the use of a 1 per cent. solution of sodium bicarbonate,¹ or of sodium chloride,² or of green malt extract³ in the making of the flour suspension. The addition of these substances is claimed to improve the separation without destroying the nutritive value of the gluten.

This process is economical; it requires very little plant and water, and has low overhead charges. About 50 per cent. of the flour solids appears in the gluten layer, which contains about 22 per cent. protein, 67 per cent. starch, and other solids; this by-product finds a valuable outlet in the manufacture of feeding-stuffs, and is used in the preparation of macaroni, semolina, and similar products.

In all the above processes the starch obtained requires purification before being used for a number of purposes, and this is carried out by washing with water, sieving, and sedimenting. The

percentage of small starch grains present is determined by the rate of flow of the starch liquor over the tables or through the vats. When the centrifuge method is employed in the purification process it is usually carried out after the primary purification in order to avoid trouble due to the gluten particles choking the filter cloth; or again, the centrifuge may be of the non-perforated type. After successive washings and sedimentation the starch cakes are filter-pressed or centrifuged in a perforated drum, and dried at 30°C ., this temperature being increased to $60\text{--}70^{\circ}\text{C}$. later, when most of the moisture has been driven off. The cakes so obtained have a brownish discoloured layer on the outside, which is scraped off and may be used for low-grade work and for adhesive-making.

In some cases the treatment of glutenous starch to obtain pure starch is carried out with water containing a small amount of acid, usually acetic acid, which exerts a dispersing action on the gluten. Sulphuric acid is sometimes used, but suffers from the disadvantage that the acid is non-volatile, whereas if acetic acid is used, any remaining traces are driven off in the drying process. Caustic soda is another excellent but non-volatile dispersing agent for gluten. If crystal starch is required, the acid treatment is often omitted, as the presence of small amounts of gluten improves the coherence of the product, whereas with very white starches containing practically no gluten it is sometimes necessary to add a small amount of white dextrin to obtain the necessary binding effect. Good crystals of maize starch (see p. 60) may, however, be prepared even when all the gluten has been removed and no dextrin added.

The Alkali Process.—In this new process, described by R. J. Dimler and co-workers,⁹ the wheat protein is dispersed by treatment with dilute caustic soda solution without affecting the starch. The alkaline liquor can be tabled or centrifuged in order to separate the starch, the former process yielding 70–80 per cent. of the starch present in the wheat as prime quality material whilst an amount of lower grade material, containing from 0.4–0.7 per cent. protein, is also obtained. This low grade material is suitable for use in conversion and fermentation industries.

If centrifugal separation is used all the starch is recovered as a single fraction containing 0.4–0.6 per cent. protein together with other alkali insoluble solids which reduce the purity to between 94 and 98 per cent. From 50–80 per cent. of the total wheat protein can be recovered, gluten having a purity from 70–90 per cent.

This process is claimed to be applicable to the manufacture of

barley, rye, oat, corn, sorghum and rice flowers so that it offers a means of utilising any variety of wheat and other cereal grains as alternatives to maize for the production of starch, according to the conditions of supply and raw material cost prevailing during any period.

The Sulphurous Acid Process.—C. T. Langford and R. Slotter¹⁰ have described a promising process which is based on a modification of the physical properties of the wheat gluten with sulphurous acid to render the gluten more amenable to treatment. The grain is steeped at 100° F. for 24 hours using 68 pints of a 0·3-0·5 per cent. solution of sulphur dioxide—a relatively high concentration—for each bushel of grain. After steeping the liquor is drained off and the grain is milled, preferably in a Buhr mill type of disintegrator rather than in a Fuss mill type. The mill liquor is passed over 26 mesh copper reels, No. 17 silk shakers and then tabled. Coarse material retained on the reels and shakers is again ground and sieved. The wheat protein by this treatment has lost its glutinous character, does not clog or deposit slime on the reels and shakers and is carried off in the outflow water from the starch tables. It can be recovered from this outflow water by settling and filter-pressing as it is somewhat ‘granular’ in condition. Its properties are somewhat different from gluten obtained by use of the older methods and it will, therefore, be unsuitable for certain classes of trade. A 55-60 per cent. yield of starch containing 0·2 per cent. protein is claimed.

Rice Starch.—The production of rice starch offers similar problems to the production of maize starch because the gluten in the rice grain does not form a coherent mass as does wheat gluten. One of the earliest methods was due to O. Jones⁶ and this, with unimportant modifications, is used to-day. Rice grains are rich in starch, and each granule is coated with a very compact layer of gluten that has to be softened before it can be removed. Granules of rice starch are very small, and take a long time to settle, hence many factories use centrifugal methods of separating the partially purified, and the purified, starch. Where settling methods are used, as much as six weeks may elapse from the time the grain enters the factory to the time the starch is ready for marketing, so that the use of centrifugal methods, although more expensive, economises both space and time.

Rice starch is generally made from the broken white grains which have been rejected for use in the foodstuffs industry, or from ‘cargo rice’, which is the grain still enclosed in the outer brown cuticle. The by-product from the latter type of raw

material is of value for cattle food, as it contains phosphorus compounds and rice oil.

The grain is fed by gravity into cement or iron vats, provided with air-agitation and fitted with perforated false bottoms. Caustic soda solution of sp. gr. 1.005 is run in until the level of the liquid is 12 to 24 in. above the grain. After standing for 24 hours, with periodic air-agitation, the liquid is withdrawn, the grains washed with water, and fresh liquor added. The steeping is continued for a further 36 to 48 hours, and then the grains are soft enough to squash by gentle pressure between thumb and finger, or the mass may have started to disintegrate. The mass of soft grains is ground with caustic soda solution of such a strength that the outflow liquor from the disintegrator has sp. gr. 1.240. Ammonia solution may be used instead of caustic soda solution; it saves half the time but is more costly.

The mass is now passed to the settling tanks, or in some factories to the centrifuges, in which case the amount of solids in suspension is kept higher than if it is to be settled. The imperforate-drum type of centrifuge is used, and after the operation has been completed any heavy fibrous matter is found against the outer wall, followed by a layer of starch containing some fine fibrous matter, whilst the last and inner layer consists of gluten admixed with some starch. The inner layer is scraped off before the main bulk of the starch is discharged.

The wet starch is agitated with water, to which is often added 0.25 per cent. of formaldehyde solution (35 per cent. strength) to inhibit fermentation, and either settled or centrifuged, and after removing the gluten layer the washing and separation processes are repeated. In some factories a bleaching process is introduced at this stage, and in others a blueing agent (see p. 276) is added in order to improve the colour of the final starch.

There is no set rule for the order in which operations for purifying the starch are carried out. In some factories screening precedes, and in others it follows the centrifugal separation. Centrifuging the starch before screening saves wear on the silk screens, as the material passing through is much less alkaline than if the order of operations is reversed. With centrifugal separation the amount of alkali present is double that used when settling is employed, and the concentration of starch is also greatly increased.

The starch liquor is adjusted to sp. gr. 1.210 and passed into draining-boxes, which have perforated bottoms and are lined with cotton fabric. In many modern plants, suction can be applied to the bottom of the boxes and, to hasten draining, air-pressure may be applied through covers fitted on the top. As it is im-

portant that no air bubbles should form in the mass, the sides of the boxes are tapped while the liquor is still free enough to liberate entrapped bubbles. When the starch has drained sufficiently to set to a solid block the boxes are discharged, and the blocks of moist starch are cut into four pieces and placed on porous plates in a crusting-stove.

In the crusting-stove the starch blocks are dried for about 48 hours at 50-60° C., then removed, and the brownish discoloured outer layer of starch scraped off and returned to one of the washing tanks. The starch-block is now ready for the final drying operation.

The drying process is very important, and must be strictly controlled, as the characteristic appearance of crystal or lump rice starch depends upon the attainment of correct drying conditions. If crystal starch is to be prepared, the blocks, after crusting and scraping, are wrapped in paper. For the first 48 hours the temperature is kept at 35° C., and the humidity of the air circulated in the drying-stove is not allowed to fall below 14 grains per cubic foot. At the end of 48 hours the temperature is raised by 3° C. in each succeeding 24 hours, and the humidity of the circulated air is allowed to fall until, when the temperature of 50° C. has been reached, practically dry air is being used. The temperature is then raised to 57-60° C. for 36-48 hours, after which the starch is removed from the stove and the paper removed. For ordinary purposes, where crystal starch is not required, a shorter drying-time and higher initial temperature may be used, as the careful drying described above is carried out solely with the object of obtaining the starch in compact lumps.

Sago.—Sago is well known as a foodstuff. It consists of the starch derived from the pith of several kinds of palm trees native to the East Indies. The typical sago palms (*Metroxylon*) grow in more or less swampy localities and die after flowering only once. The species generally chosen are: *Sagus rumphii*, *S. farinifera*, *S. borassus flaballiformis*, *S. laevus* and *Arenga saccharifera*. *S. laevus* furnishes most of the material used in export as it grows chiefly in the western part of the East Indies and is thus more readily transported to Singapore whereas *S. rumphii* growing in the eastern parts, including New Guinea, furnishes the product for local consumption. Some of the *Cycads* (*Cycas circinalis* and *C. revoluta*) are known as false sago palms, and considerable quantities of sago starch are made from them.

The palm requires a moist soil and flowers when it is about 7 or 8 years old. Just before this takes place the whole stem, which may be 1½-3 ft. in diameter at the base and often over

30 ft. high, is loaded with starch. Three trunks about 15 ft. high and 20 in. in diameter will then yield about as much starch as an acre of wheat. The trees are felled when about 25-30 ft. high and the trunks stripped of leaves and cut into lengths of about 3 ft. for ease of handling. The 2 in. thick outer woody rind is slit lengthways, the pith removed with a wooden hoe and beaten with water. The milky starch suspension is filtered through a rough sieve consisting of mats of palm leaf stems to remove the fibrous material of the pith. The pith is subjected to several washings and strainings, the starch milk being run into troughs where the starch settles out. These operations are carried out at the growing site. Further purification takes place in the factories, re-suspension in water, filtering through cloth and another simple tabling process being carried out. The moist starch is either dried on mats in the sun, which brings about concurrent drying and bleaching of the slight colour shown by the newly deposited moist starch, bagged, shipped as 'sago flour' or converted into pearl sago. To make the latter product the moist starch cake is pressed through a perforated sheet of iron or a coarse screen. The pellets of starch are put into a shallow hammock-shaped cloth to which a circular swinging motion can be imparted. Swinging this contraption in the correct manner imparts a rotary motion to the pellets which, providing the moisture content is correct, assume a roughly spherical shape, the process being rather akin to pill-rolling. The pellets are compact enough to screen to remove fine particles and large aggregates. The sieved pearls are then roasted in shallow metal pans which partly gelatinises and dries the sago pearls.

Artificial 'sago' is produced in a similar manner to the genuine article, but other starches may be used. Of these potato starch has been employed in Germany. The moist starch is pressed through circular orifices in a plate which is vibrated to detach the extruded starch in the form of nodules. These small cylinders are next rounded by tumbling them in a revolving barrel, with a little powdered starch to prevent sticking, graded to size and then subjected to hot steam on trays for a short time to produce a thin surface film of gelatinised starch. The steam is shut off when this has been accomplished and hot air passed over the trays to dry the gelatinised layer. The simulation of real sago has been carried still further by slightly tinting the pearls to a brown shade by roasting or to a yellow by the use of a trace of caramel. According to Rehwald red iron oxide is sometimes employed to produce a reddish tint. Pearl tapioca is made in a somewhat similar manner to pearl sago.

In Java an unappetising tasting and looking sago is the chief food of the natives who make it from the Gomuti palm, *Arenga saccharifera*. Another 'sago' is made from sweet potato starch often blended with other starches.

REFERENCES

1. KLOPPER, G.P. 102,465. (Lapsed.)
2. — G.P. 201,969.
3. — E.P. 11,159, 1907; E.P. 19,726, 1908. (Both lapsed.)
4. A. E. WILLIAMS, *Ind. Chem.*, 1930, **6**, 387.
5. D. B. JONES, *Cereal Chem.*, 1937, **14**, 771.
6. O. JONES, E.P. 8,488, 1840.
7. A. SCHHUKIN, *Naukh-Agron. Zhurnal [Russia]*, 1926, **3**, 379.
8. M. M. McMASTERS and G. E. HILBERT, *Cereal Chem.*, 1944, **21**, 258.
9. R. J. DIMLER *et al.*, *Cereal Chem.*, 1944, **21**, 430.
10. C. T. LANGFORD and R. SLOTTER, 'Wheat Starch Programme of the Northern Regional Laboratories', paper presented at National Farm Chemurgic Council, Seattle, 1942, via. R. W. KERR, 'Chemistry and Industry of Starch', N.Y., 1944.

ADDITIONAL REFERENCES

- A. RICHE, *J. pharm. chim.*, 1880, **1**, 137. (Describes fermentation process for making maize starch.)
- L. BONDONNEAU, *Bull. Soc. encour. ind. nat.*, 1893, **92**, 849. (Trough-settling superior to tank-settling.)
- E. LECONTE, *Elektrochem. Zeit.*, 1904, **11**, 113. (Preparation and purification of rice starch using electric current.)
- K. HEMBD, *Zeit. Spiritusind.*, 1919, **42**, 395. (Good starch deposits more quickly than poor starch.)
- F. B. WISE, *Assoc. Rice Millers*, 1921, **1**, 18. (Detailed description of rice-starch manufacture.)
- O. K. A. KRIZKOVSKY, *Zeit. Spiritusind.*, 1923, **46**, 123. (Detailed description of Martin's method.)
- E. PAROW, *ibid.*, 1923, **46**, 1, 6, 12, 17, 23. (Describes machinery for starch manufacture.)
- A. P. WEST and O. A. CRUZ, *Philippine J. Sci.*, 1933, **52**, 1. (Rice-starch manufacture in the Philippines.)
- H. BADER, *Ann. brass. distill.*, 1934, **32**, 113. (Rice starch.)
- O. K. A. KRIZKOVSKY, *Chem.-Ztg.*, 1928, **52**, 425, 466, 486, 526. (Maize starch.)
- A. E. WILLIAMS, *Ind. Chem.*, 1933, **9**, 129. (Maize starch.)
- ANON, *Chem. Trade J.*, 1935, 409; *Gel. Leim u. Klebst.*, 1935, 168. (Rice starch, Continental methods.)
- S. MIZAKA and K. HAYASKI, *J. Soc. Trop. Agric.*, 1936, **8**, 185. (Amylosynthase from Formosa rice.)
- W. KRÖNER, *Zeit. Spiritusind.*, 1938, **61**, 235, 243, 253. (Significance of the starch-industry from viewpoint of food supply.)
- M. SOBORNOV, *Spirto-Voctohnaya Prom.*, 1938, **15**, 29. (The starch-content of cereals cannot be estimated from the density.)
- F. B. DEHN, E.P. 277,400, 1926. (Counter-current principle in maize starch production.)
- E. C. R. MARKS, E.P. 277,572, 1927. (As above, using SO₂ in the water.)

- E. SCHLÜTER, E.P. 225,101, 4 '3 1924. (Lapsed.) (Production of rice starch.)
- H. KAUTZ, SWISS P. 115,305, 1925. (Manufacture of rice starch.)
- INTERNATIONAL PAT. DEVEL. CO., Fr.P. 813,220, 28 '5 1937; Fr.P. 813,221. (Maize starch and gluten separated by aeration of partly purified starch suspension.)
- A. E. STALEY MFG. CO., U.S.P. 2,058,683. (Manufacture of maize starch.)
- K. SUBBA RAO, *Current Science*, 1939, **8**, 250. (The sorption-desorption cycle of polished rice followed. Absorption maximum increased from one cycle to the next.)
- F. J. JEFFERIES (to Int. Pats. Desel. Co.), U.S.P. 2,098,293. (Preparation of starch as dustless flakes for malting purposes.)
- CORN PRODUCTS REFIN. CO., F.P. 844,308, 24 '7 1939. (Plant described for manufacture of maize starch.)
- E.P. 530,226; Conv. 11/7 1938; 6 12/1940. (Starch dried by disintegration in stream of hot gas at a temperature above the gel point.)
- U.S.P. 2,228,717. (Corn steeped in water containing 0.05-0.1 per cent. chlorobenzene or chlorotoluene and a mixture of 2 parts NaHSO_3 and 1 part NH_4HSO_3 to give SO_2 content of 0.12 per cent.)
- P. CHATSKIL, *Spirto-Vocchochnaya. Prom.*, 1939, **16**, No. 2, 36. (Nomograms for starch-content of barley and rye.)
- L. P. BAUER, U.S.P. 1,099,276, 1914. (Drying of starch.)
- JEFFRIES, U.S.P. 1,007,782, 1,007,783, 1911.
- R. W. CALLAGHAN and G. W. ELVERUM, U.S.P. 2,388,902, 1945. (Preparation of wheat starch from flour.)
- A. L. SHEWFEELT and G. A. ADAMS, 1945, *Can. J. Research*, **23F**, 373-82. (A rapid method of separation of starch from wheat flour described.)
- A. L. SHEWFEELT and G. A. ADAMS, 1946, *Can. J. Research*, **24F**, 136-39. (Separation of wheat starch from flours from various types of wheat.)
- R. W. CALLAGHAN and R. H. SCHILLING, U.S.P. 2,418,621, 1947. (New wet process for improved wheat starch process.)
- R. H. SCHILLING, U.S.P. 2,418,660, 1947. (New wheat starch process using 0.25-3.0 per cent. of soluble metal nitrate to inhibit fermentation, prevent gluten denaturing and buffer pH to 5-6.)
- M. I. KNYAGINICHEV, U.S.S.R. Pat. 66,225, 1946. (Starch extracted from grain with sodium salicylate and precipitated therefrom with acetone.)
- W. J. EVA, J. LEVI and J. A. ANDERSON, *Can. J. Research*, 1943, **21C**, 173-9. (Starch content of Western Canadian wheat.)
- J. A. ANDERSON and W. J. EVA, *Can. J. Research*, 1943, **21C**, 323-31. (Starch content of Western Canadian wheat, its estimation from protein content and some estimated data.)
- F. E. HORAN and M. F. HEIDER, *Cereal Chem.*, 1946, **23**, 492-503. (Typical analytical figures for sorghum grain and properties of the starch discussed.)
- C. HAGEN, U.S.P. 2,144,333, 17 '1 '39; Appl. 8/4/37. (Apparatus for drying moist starch in a vac. chamber is described.)
- A. J. BULFER, U.S.P. 2,401,813, 11 '6 '46; Appl., 13 '12 '43. (Thermophilic bacteria killed by drying to 1-2 per cent. water at 55-60° C. then roasting at 115-125° C. for 1-3 hours.)
- KARPER, *Chemurgic Digest*, 1946, **5**, No. 3, 65. (Discusses research on waxy sorghum starches and use for adhesives.)
- HANS RITTER, D.R.P., 740,844, 9 '9 1943 (cl. 89 K.2.). (Alkali process as used for rice starch manufacture used to make barley starch.)
- HANS RITTER, D.R.P., 742,638, 21 '10 1943 (cl. 89 K.2.). (Separation of starch and gluten from rye described.)
- C. B. PATEL, *Current Sci.*, 1943, **12**, 325. (Analysis of *Panicum milaceum* grain, its use in manufacture of starch described. Starch has similar properties to maize starch.)
- J. L. SARIN and M. H. QURESHI, *Ind. Eng. Chem.*, 1938, **30**, 1318. (Analysis and properties of Grain and Grain starch.)

CHAPTER 3

CORN STARCH MANUFACTURE*

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I. Introduction.—Corn starch is manufactured principally in the Americas and is the chief industrial starch of the western hemisphere. The United States is the largest producer and the manufacturing plants are located in the north central section of the country, referred to as the corn belt. The States of Iowa and Illinois produce more grain and more corn starch than any other section of country.

The corn starch industry was pioneered by Kingsford¹ and by Duryea and dates from about the middle of the last century. Their factories were located in the State of New York. Following the agricultural development of the great prairies of the Mississippi River basin, the industry moved westward. In more recent time, it appears to be profitable to grow corn for the feeding of livestock and about 85 per cent. of the crop remains on the farms to be used for seeding and for feeding. It has become unprofitable to transport the grain for starch manufacture to the industrial regions on the seaboard.

Many of the corn starch factories located in central and South America are owned or operated by corporations producing corn starch in the United States. One of these also was engaged in the manufacture of corn starch, at least before the war, in factories located in Great Britain, France, Holland, Czechoslovakia, Italy, Germany and Korea. Corn grown locally and in South Africa and Argentina was the principal source of supply.

Of the 2,750,000,000 to 3,000,000,000 bushels of corn grown annually in the United States, only about 3 per cent. is used for milling to make starch and products derived from starch.² About one half of this amount, or 1.5 per cent. of the crop is milled for making starch to be sold as such, the other 1.5 per cent. is used for making derived products such as sugars, syrups and dextrans. Owing to the insignificant fractional part of the corn crop which is utilised for milling starch, rather limited attention

* *Corn* and *corn starch* are now generally known as *maize* and *maize starch* respectively in Great Britain. J. A. R.)

has been given to the cultivation of a variety of corn best suited for the manufacture of starch. The emphasis in genetical studies has been, in general, to produce hybrids which will give the highest yield of grain per acre for particular soil and climatic conditions. A soft, floury type of grain from which the starch is readily milled with little physical or chemical degradation of the carbohydrate is usually less resistant to destructive biological agents than a tougher, hornier variety. Often, the white varieties of grain, which yield a starch of brilliant whiteness grow better in regions to the south of the corn belt where the season for growth and maturing is longer. In recent years the trend has been for farmers to plant a more horny type of grain, the characteristics of which will be compared in the following section.

The yield and quality of starch manufactured from a given weight of grain has not only been maintained but actually increased in recent years against the adverse trend in the less desirable type of grain supplied to the millers. This reflects to some extent the study and research which has been devoted to this manufacturing process.*

Corn,^{3, 4} of which more than 500 varieties are known, is native to the Americas. It has also been introduced to and grown extensively in many sections of the Eastern Hemisphere by Europeans. In northern latitudes the seed is planted during late April or early May. The plant grows rapidly in deep fertile, friable loam soils when the climate is warm and humid. Not only are sunshine and warm days required, but for the most rapid development, warmth during the night is also desirable. These requisites are fulfilled by the climate of the American corn belt. The plant is easily injured by drought and winds, especially when the tassels and ears (on which the grain grows) are forming. Although corn is of the family of grasses, the long blade-like leaves may be cut to shreds by arid winds such as frequently prevail on the plains west of the corn belt. The plant rises above ground in several weeks time to a height of 7 to 10 ft., on which a pithy, cellulose-containing cob develops. On these, some 3 to 6 to a stalk, the grain grows protected by a sheath of leaves. Some 20 weeks after planting, the grain may be sufficiently matured and the ear is then removed from the stalk and husked. The grain may be stored locally on the cob or shelled and transported to granaries from whence it is sent to the mills.

* Most of the American supply of corn starch is milled by ten companies. All are equipped with laboratories devoted to fundamental and applied study of starch and its manufacture. In addition, the industry as a whole supports the Corn Industries Research Foundation which maintains fellowships for the study of problems related to the industry.

Being a seed, corn may be stored for future use over extended periods of time if allowed to mature fully and if kept in a dry state. During maturation the moisture in the grain drops to a normal of about 20 per cent. During storage the moisture content is reduced further depending on the relative humidity under which it is stored. Moisture contents as low as 10 per cent. are not uncommon. On the average, however, the moisture content of grain coming to the mills a month or two after harvest is about 18 to 20 per cent. Thereafter, until the harvest season the year following, the moisture content of the current crop arriving at the mills falls off to about 13 to 15 per cent. Below 18 per cent. moisture the enzyme systems capable of degrading native starch are comparatively dormant. However, as the grain dehydrates it becomes tougher and less readily re-hydrated in wet milling processes. The intensity of the milling procedures may be stepped up accordingly with the result that the starch granules may be injured or their components slightly degraded when old, dry corn is used. Therefore, in practice, a starch of higher viscosity may be produced from new corn or from corn which has not had an opportunity to mature fully. The writer has observed the production of starch, which had a paste consistency of 160 by Scott Test, from immature corn grain, whereas starch from mature corn usually gives a value of about 90.

No significant change in the ratio of amylose to amylopectin (constituent polymers of starch) has been observed in corn starch during maturation of the grain or during normal storage. The total starch content does, however, increase during the early stages of the maturation process. Immature corn, or grain of high moisture content for other reasons, may be dried for future use, as indicated below.

From the foregoing, it should be evident that the operation of corn starch factories is not disrupted because of seasonal changes in the availability or supply of raw material such as is normally the case for potato or tapioca starch factories.

II. The Corn Grain.—Corn grain as now processed in the United States shows the general analysis.⁵ (See Table I on page 36.)

On a dry weight basis, the grain now milled contains between 66 and 70 per cent. starch although some varieties contain 75 per cent. and higher.

The protein of corn consists chiefly of the relatively water-insoluble zein and zeinin. They are appreciably soluble in acid, more soluble in alkalis such as sodium and potassium hydroxides, and are dispersed in aqueous solutions of soaps. Zein is soluble

in aqueous alcohol. A minor amount of albumins is also present in corn.

TABLE I
Composition of Corn Grain

	<i>Per cent.</i>	<i>lb. per bu.</i>
Moisture	18.5	10.36 ✓
Starch	55.5	31.08
Protein	8.2	4.59
Oil	3.0*	1.68
Fibre	2.4	1.34
Ash	1.5	0.84
Pentosans	5.1	2.86
Water soluble and undetermined	5.8	3.25
	<hr/> 100.00	<hr/> 56.00

The oil consists principally of low melting point, glycerides of palmitic, oleic, and linoleic acids.

The ash of corn grain is given⁶ as follows :

TABLE II
The Ash of Corn Grain

	<i>Per cent.</i>
P ₂ O	47.60
K ₂ O	29.47
MgO	14.39
CaO	1.90
SiO ₂	2.27
Na ₂ O	1.43
Fe ₂ O ₃ and Al ₂ O ₃	1.22
SO ₃	0.67
Cl (in chlorides)	0.78

A large part of the phosphorus is present as salts of phytic acid which are soluble in acidulated water.

The phytin content in corn increases as growth progresses, reaching a maximum in the seventh week when about 25 mg. of phytin phosphorus is formed daily per ear. At full maturity, phytin phosphorus amounts to 0.27 per cent. or 88 per cent. of the total phosphorus according to Early and DeTurk.⁷

The water soluble extract of grain is approximately pH 6.0-6.5. About one-third of the dry substance of the extract is composed of low molecular weight carbohydrates. These may be fermented by bacteria associated with grain when steeped in the warm acidulated water used in the early stages of wet milling. The chief product of fermentation in this case is lactic acid. The acids tend to hydrate the protein of the grain and to solubilise the alkaline

* On a dry weight basis, corn now being milled has an average oil content of 4.5 per cent. which is 3.67 per cent. at 18.5 per cent. moisture.

earth salts. The phytates may be split to phosphates and inositol; the proteins into the usual degradation products, peptides, amino acids and NH_3 .

The corn grain may be considered as comprised of four regions : (a) an outer hull which encases the other three regions, (b) the embryo, or germ, which is located near the tip of the grain behind the tip cap, (c) the crown, that part of the endosperm which is light in colour and is located at the opposite end from the germ (in some varieties it may extend down to and around the germ ; see Fig. 3:1), and (d) the remainder of the endosperm which is more intensely coloured than other regions in yellow varieties of corn. In addition, the hull, or pericarp, may be separated from the rest of the grain by a very thin layer of glutinous material.

The hulls contain insoluble, non-starchy carbohydrates and inorganic constituents and are readily loosened and removed by soaking the grain in warm water followed by passage through coarse mills and then over screens.

The chief constituent of the germ is the low melting point fats as is shown in the following table of analysis for average samples now being milled.⁶

TABLE III
Composition of Corn Germ

	<i>Per cent.</i>
Moisture	1·6
Oil	56·5
Protein	11·5
Fibre	9·0
Starch	8·0
Water Soluble	2·6
Mineral Matter	1·0
Pentosans and undetermined	9·8

Owing principally to the high oil content, the germ has a lower specific gravity than the endosperm and because of this the germs in roughly ground, steeped corn may be separated from the rest of the grist by levitation. After washing and drying the germ, most of the oil may be pressed out by the use of heated expellers or removed by extraction with solvents.

The crown region of the endosperm contains starch which is packed quite loosely in contrast to the tightly held starch embedded in the horny regions of the endosperm. Crown starch consists primarily of round granules which are readily loosened from each other by a very limited steeping period in warm water and a moderate amount of milling. Cross-sections of layers of the horny regions show smaller, polygonal starch granules embedded in sheets of glutinous material. The appearance is that of a

TABLE IV
Characteristics and Properties of various Corn Samples

Variety	Test Weight Lb./bu.	Spec. Gravity at 70° F.	Starch %	Protein %	Oil %	Ash %	Cold Water Extract Starch from Non-steeped Corn			
							% Solids	pH	Yield, g.	Scott Test
1. Mandan	54.5	1.11	63.28	15.15	6.57	1.88	6.95	6.5	57	140
2. Exp. soft yellow	54.6	1.16	70.02	13.90	4.47	1.42	8.45	6.2	62	113
3. Illinois, com- mercial type rough dent	54.0	1.16	70.85	11.70	4.99	1.67	8.20	6.2	69	112
4. Ill. low protein	57.0	1.21	75.28	8.23	4.41	1.45	7.15	6.3	43	101
5. Mixed, milling grade	56.5	1.21	73.22	10.83	4.51	1.30	8.12	6.2	36	109
6. Oklahoma, Hickory King	57.0	1.21	70.52	12.41	5.06	1.58	8.09	6.3	32	110
7. Champion, White Pearl	59.3	1.25	71.75	11.60	5.17	1.23	8.20	6.3	25	97
8. Commercial type of utility	60.5	1.26	69.96	12.60	4.87	1.40	7.95	6.3	21	83
9. Ill. high protein	59.0	1.25	60.02	20.20	4.89	1.75	8.70	6.3	14	80
10. Ill. Hybrid No. 998	60.2	1.27	68.82	11.70	6.32	1.40	8.65	6.3	15	65

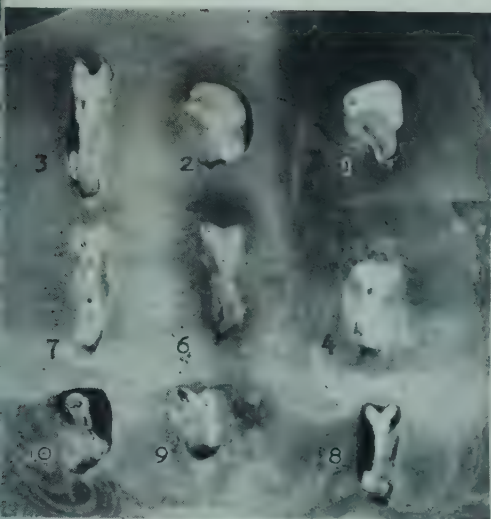


FIG. 3:1. Cross-sections of corn grains.

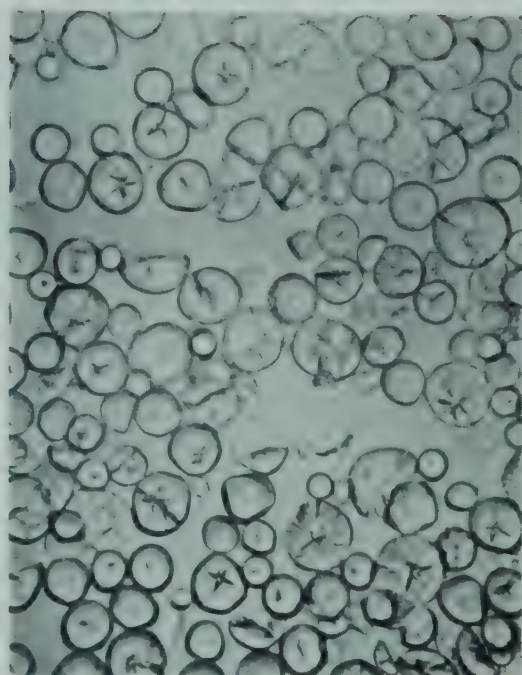


FIG. 3:2. Floury corn starch.

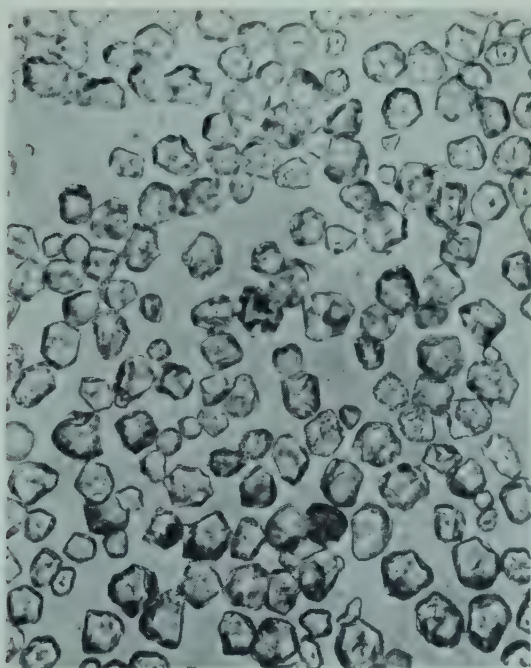


FIG. 3:3. Horny corn starch.

cross-section of concrete, the 'crushed rock corresponding to the starch and the cement to the gluten. Penetration of pure water into these regions of the grain is extremely slow. Indeed, loosening of the starch in the horny regions can only be accomplished with the efficiency demanded in practice by the addition of solvating agents such as acid or alkali to the steeping liquor or by enzymic action, followed by comparatively intensive grinding operations. The acidity and time of contact necessary to hydrate the horny gluten and grinding required to expose the starch granules so they may be removed from the sheets of gluten is sufficient to cause material degeneration of the starch when these conditions are applied to the crown regions.

Distinguishing characteristics for many varieties of corn grain are the proportion of crown starch to horny and the shape of the crown region. In the more floury types, the crown starch predominates. Corn sample No. 2 (Table IV), an experimental variety, a cross-section of which is shown in Fig. 3:1, is an extreme example of the floury type. The starch obtained from this corn is shown in Fig. 3:2. Some of the floury types of grain contract in the crown region during the maturing period so as to show a very noticeable indentation. These are classed as Dent Corns. The tougher varieties are classed as Smooth Dent and as Flint Corns. An extreme example of the horny type of corn is sample No. 10 which is Hybrid No. 998, a cross between an American Utility type (medium horny) and the Russian Kutias, which has no crown starch whatsoever. The starch obtained from Hybrid No. 998 is shown in Fig. 3:3.

Corn now arriving at the North American mills is a mixture of the various hybrids grown locally and these are medium horny varieties. This is sample No. 5 in the discussion which follows.

Ten samples of corn as listed in Table IV, were treated as follows. Three hundred grams of corn were ground through a Corona Mill which consists of a screw feed to two vertical, rough metal grinding plates. This grist was triturated with water in a mortar to make a soggy mass. A slurry was made using in all 750 ml. of water. The coarse particles were collected on a No. 30 mesh screen and were then reground and again rubbed up in a mortar with liquor from the first grind. The finer particles were ground and rubbed in a mortar twice more, another 750 ml. of water being used on the third grinding and sieving operation. The fine grist was collected and passed through No. 17 bolting silk sieves (about 160 mesh). All residues were washed in turn with an additional 300 ml. of water. The liquors passing through the silk sieves were collected, run over a laboratory starch table in

order to sediment the starch which was then collected, washed with distilled water and dried.

Table IV, p. 38, shows the high, hot paste viscosity obtained from

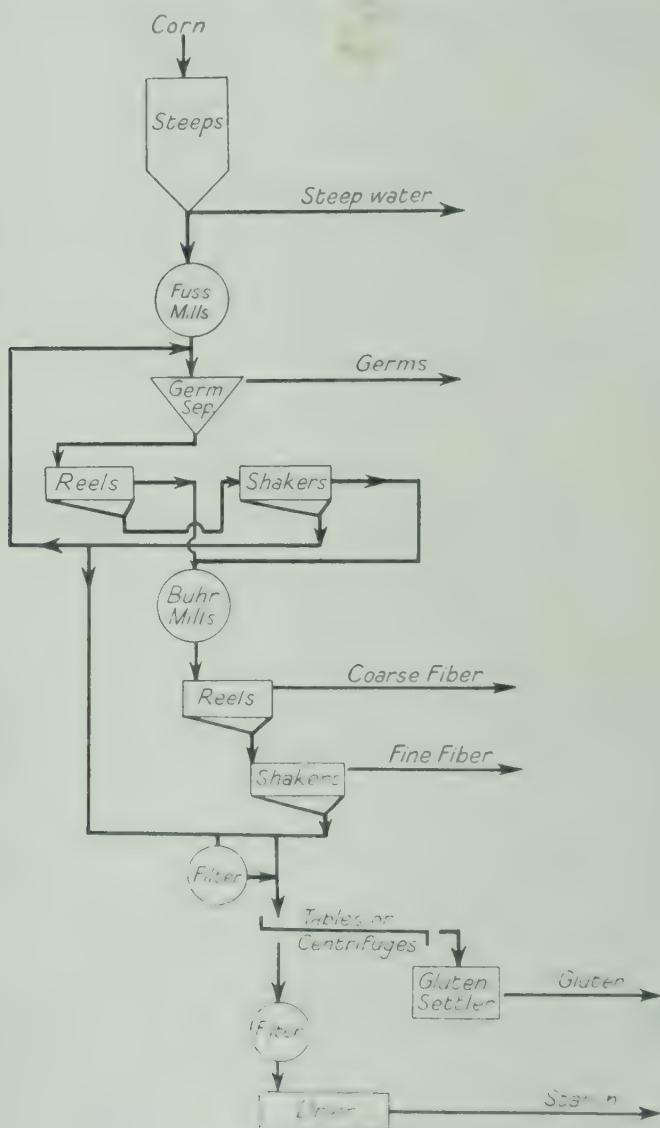


Fig. 3:4.—Wet milling of corn.

the prime starch in the floury varieties. The viscosity falls off together with the yield as one passes to the more horny samples.

More comparable yields of starch were obtained from the various types by steeping the corn samples in steeping liquor used in industrial practice. This is gluten overflow water, described subsequently, to which SO_2 is added to give a concen-

tration of 0.15 per cent. Various steeping times at 50° C. were used as are indicated in Table V. It will be observed that even though steeping times have been adjusted so as to obtain comparative yields of starch with a limited amount of laboratory grinding, the floury varieties give a starch of materially reduced paste viscosity. The paste viscosity of the most horny varieties were improved by the steeping period which permitted the more ready removal of starch from the residue. However, the highest paste viscosities were obtained in the laboratory, under the conditions used, from the intermediate samples which were steeped 24 to 40 hours.

TABLE V
Steeped Corn Samples

<i>Variety.</i>	<i>Corn Steeped, Hrs.</i>	<i>Starch from Steeped Corn Yield, g.</i>	<i>Scott Test.</i>
1. Mandan	16	167	67
2. Exp. soft yellow	16	159	82
3. Illinois, commercial type rough dent	20	167	97
4. Ill. low protein	24	160	107
5. Mixed, milling grade	40	161	104
6. Oklahoma, Hickory King	40	143	130
7. Champion, White Pearl	40	142	108
8. Commercial type of utility	40	149	103
9. Ill. high protein	88	83	95
10. Ill. Hybrid No. 998	65	144	93

Modern practice demands a considerably higher yield of starch than indicated above and values as high as 67 per cent. are commonly reported. Milling operations are, therefore, made rather severe in order to recover the major share of the horny starch within the grain. The result is that the paste viscosity of the starch by Scott Test⁸ is about 90.

Horniness is not necessarily related to the protein content of the grain. More likely, it is due to the physical state of the water insoluble proteins in the endosperm. Two other extreme types of hybrids are interesting to note at this point, an Illinois high and low oil corn grain.

TABLE VI
Comparison of High and Low Oil Content Corn

	<i>Starch, %</i>	<i>Protein, %</i>	<i>Oil, %</i>	<i>Ash, %</i>	<i>Test Weight lb./bu.</i>
Illinois Low Oil Hybrid	69.57	12.29	1.24	1.39	53.0
Illinois High Oil Hybrid	54.62	13.74	12.23	1.83	58.5

It will be observed that the high oil corn is the hornier for, in spite of the fact that it contains about ten times as much oil, its test weight per bushel (and specific gravity) is considerably higher than the low oil hybrid.

The above conclusions are borne out by the recent work of Cox, MacMasters, and Hilbert.⁹ who find the following analyses for the horny and flourey endosperm of Reid Yellow Dent Corn.

TABLE VII
Analysis of Horny and Flourey Regions of Dent Corn

<i>Constituent</i>	<i>Horny Endosperm</i>	<i>Flourey Endosperm</i>
Protein ($N \times 6.25$)	13.25	7.69
Alcohol soluble N	1.49	0.64
Starch	80.4	85.6
Sugar	0.47	0.52
Oil (petroleum ether extract)	0.73	0.33
Ash	0.27	0.35

Although the protein content of the horny region is nearly twice that of the flourey, nevertheless, the latter contains a substantial percentage of protein. The oil content of the horny region is more than twice that of the flourey. The protein network, which appears as strands after cross-sectioning, is birefringent indicating that molecules in the network are oriented. These workers suggest that powerful binding forces are operative in these crystalline regions which resist solvation and account for the toughness of the protein network.

Because the wet-milling industry requires a substantial portion of the corn grain which is placed on the market, it frequently becomes necessary to mill the lower grades of corn.* Damp corn may be mixed with better grades and milled immediately or it may be dried, either at the corn elevators or at the mills. If damp corn is held in storage biochemical activity soon develops to the point where the temperature of grain increases. If the action is not checked, as by aeration, or 'turning over', the grain may become so hot as to be rendered worthless for milling. As a precaution, many mills equip their storage tanks with thermo-recorders in order to be informed when, and if, the initial phases of biochemical activity have started.

The deterioration of the grain usually starts from a fungal growth, the mycelia of which readily penetrate the kernel near the germ, digest the contents of the latter and then invade the endosperm. A usual characteristic of damaged corn is an oil content below normal.

On the assumption that more or less undesirable biological activity has existed in low grade, damaged corn, a test has been proposed to differentiate grades by differences in the titratable

* For grain standards see *Handbook of Official Grain Standards of the United States* published by U.S. Bureau of Agricultural Economics.

acidity of the whole kernel.¹⁰ Ten grams of ground corn are titrated in a water suspension with 0.01 N NaOH and the result expressed in ml. Number 1, sound corn, tests approximately 10 ml. whereas very low grade corn may test as high as 50 ml. At least part of the acidity is due to fatty acids which arise from the hydrolysis of the fats in the germ. Bartling¹⁰ finds that the oil expressed from the germ of mouldy corn contains more free fatty acids than the oil from sound germs.

When immature, mouldy or wet corn is dried for transit or storage before wet milling, certain changes are induced in the gluten which complicate the separation processes. Cox, MacMasters and Hilbert⁹ found that when corn samples are dried at 180° to 200° F., the protein of the endosperm (the network holding the starch particles) did not swell to the same extent as corn not artificially dried when both corn samples were soaked in dilute sulphurous acid for 24 hours at 49° C. In addition, the starch was held more tenaciously by the protein matrix in the artificially dried sample and although protein dispersal appeared to be normal during the soaking period, the disintegrating matrix left pieces which adhered closely to the starch granules. Another sample of corn, artificially dried at 120° F., appeared intermediate in behaviour between corn dried in the field and that dried at 180° to 200° F.

Low grade corn which has been treated at the grain elevators by procedures involving kiln drying, and without due regard to the principles disclosed above, is an undesirable raw material for the miller.

III. Cleaning and Steeping.—The corn grain is delivered to the miller by railroad in box cars. In many mills the grains are unloaded by power shovels although in some mills the car is run onto a platform which tilts it to empty by gravity flow. The grain falls into a pit from whence it is carried by screw conveyor to a bucket elevator which raises it to the top of a cleaning or winnowing mill. Here, by air currents, the dust, chaff, broken grain particles and other light material are removed and collected. Screens are used to remove stray cobs and other extraneous material and magnetic devices may be used to remove metallic objects which may have fallen into the grain in transit.

Normally, the corn is transported to concrete bins which may hold as many as 40 carloads each. The usual custom is to maintain about a 30-day supply of grain although, occasionally, the supply held in storage is less. If wet grain is received and drying facilities are inadequate it is generally milled directly.

From the large storage bins the grain is transported by elevator

and by continuous belt conveyor to a weighing device where the grain is tripped into hopper bins which supply the first units of the wet milling system. Wet milling is the common practice, a brief outline of which is shown in Fig. 3:4. For this purpose, the corn is first soaked in warm water for various periods of time and under other conditions which are varied with the nature of the corn. This procedure is called steeping.

Several objects are to be achieved in the steeping process, the most important of which are as follows :

1. To soften the kernel so that the various components of the grain, such as the hull and fiber, the germ (which contains nearly all of the oil), the gluten and the starch, may be separated from each other with a high degree of efficiency.

2. To remove a portion, at least, of grain components which are soluble in warm water.

3. To reduce or inhibit the activity of micro-organisms that are brought into the mills on the grain.

4. To complete the cleansing of the grain.

The softening action is by far the most important and complex ; important because the efficiency of the milling operations in respect to the recovery of components depends upon it and complex because of the difference in chemical composition of the various grain constituents or parts which are to be conditioned. Hydration is an important factor of the softening action and the water content of the corn increases rapidly at first to about 35-40 per cent. and then levels off at about 43 to 45 per cent. At this level, the hulls and germs are readily removed by a coarse grinding operation. However, even at a satisfactory moisture level the starch cannot necessarily be loosened from the gluten in which it is embedded and it is apparent that : (a) either some change in the physical nature of the protein is required, or (b) the solvation of a cementing substance holding the granules in the protein is necessitated. Existing information, given below, favours the former view, that the protein itself is the cementing agent. The germs are separated first from the coarse grist by flotation. This is made possible by the lower specific gravity of this component which is due to its oil content, the water which it takes up during steeping and by the removal of a portion of the water soluble solids in the steeps.

After removal of the hulls by passage over screens and a fine grinding to loosen the starch from the gluten the latter two are separated from each other by sedimenting the starch and floating the gluten. Even though the starch has been loosened from the protein network of the kernel efficient sedimentation of the starch

can be accomplished only if the steeping operation has been properly performed. The physical state of the gluten is important as is also the presence of a sufficient quantity of electrolytes which should not be unduly removed by leaching in the steeps.

Various agents have been suggested and used to limit microbiological activity. However, SO_2 is now almost universally employed. This is due to its low cost, its pronounced germicidal properties under controlled conditions and because it may contribute to other favourable actions which are desirable in steeping. Lactic acid bacteria are the type most commonly found in steeping media. Some yeast-like organisms are present which may develop at the lower temperatures used in subsequent milling and separation procedures and fungal growth usually ensues where moisture and temperature are suitable and if a sufficient concentration of SO_2 , or other germicide, is not maintained. Thus if microbiological activity is permitted, the fermentable carbohydrate, such as the soluble sugars, may be converted to lactic acid, acetic acid, alcohol and other products. Some of the organisms can hydrolyse, or convert, accessible protein into its degradation products. A part of this biochemical activity is desirable. Native protein which dissolves or disperses in the steepwater coagulates or denatures to form an insulating coat on the heating elements of evaporators used to concentrate and recover the soluble corn solids after steeping. A partial degradation to a non-coagulable stage is therefore desirable. However, if this activity is uncontrolled or too rapid, large amounts of native protein will be dissolved, maintaining a saturated solution in respect to the protein. Meanwhile, the dissolved protein is being split into low molecular weight bodies. The degradation of the protein will proceed into the last stages and amino acids and nitrogenous bases may permeate the starch and very materially increase the difficulty of obtaining a pure starch in the final washing stages of the wet milling process. Adsorbed nitrogenous material on starch is undesirable when the starch is converted into sugars and syrups in manufacturing units following the milling process. These materials tend to change, unpredictably, the acid activity used in the hydrolysis and favour the creation of coloured bodies which lower the quality of the end products. Some biochemical activity is desirable in respect to lactic acid production. Lactic acid tends to soften the gluten in the steeping process⁹ and being non-volatile it is retained by the steepwater during evaporation after steeping, thereby tending to hold magnesium and calcium salts, also present in the water, in solution as acid salts. Otherwise, these salts form insoluble crusts,

or scale on the heating units of the evaporators. However, the creation of large amounts of lactic acid is undesirable for several reasons: the solvation of native protein is promoted to an undesirable extent and the lactate ion has an adverse effect on the sedimentation of starch from finely ground mixtures of starch and gluten.

The presence of soluble phosphates, formed in part from phytin, is desirable since these electrolytes increase the sedimentation rate of starch in the presence of finely ground, hydrated gluten.

Practical operators in the mills sum these considerations by stating that an object of steeping is an efficient removal of substances in corn originally soluble in water without the creation of undesirable new soluble material.

Killinger¹¹ has discussed the control and use of SO_2 in respect to its germicidal properties in wet milling. Free SO_2 , or sulphurous acid, is an effective inhibiting agent for the organisms studied at relatively low concentrations (0.02 to 0.03 per cent.) and its efficiency is markedly increased by raising the temperature over the range from about 30° to 50° C. However, a considerable portion of the SO_2 added to process waters does not remain free; it reacts to form bisulphite and to form addition compounds with amino groups, ketoses¹² and with carbohydrates, possibly through the aldehyde group and these combined forms are very much less effective sterilising agents. A determination of SO_2 in process water by titration with standard iodine solution, a procedure formerly used in the industry, conveys little information on the relative germicidal properties of the SO_2 present. The determination of free SO_2 by extraction with benzene is recommended. The efficiency of the germicide is reported to be not necessarily attributed to the acidity (pH) required to maintain the SO_2 in the 'free' state.

The function of SO_2 as a steeping agent has been investigated by Cox, MacMasters and Hilbert.⁹ These investigators showed that starch is embedded in and tightly held by a protein network which is birefringent. During steeping the network swells and tends to form tiny globules of hydrated protein. With time, the protein loses its birefringence, tends to disperse and finally the undispersed portion is so weak that after removal of the starch granules it collapses against the cell walls and shows little evidence of the original network of films. SO_2 greatly accelerates this process. It was found impossible to steep corn satisfactorily by soaking the grain in distilled water at 49° C. for 24 hours and after milling only 64 per cent. starch recovery was obtained. SO_2 accelerated the steeping action in proportion to the amount

added as is indicated in Table VIII, p. 60. However, the addition of acetic acid, added in an amount equivalent to 0.2 per cent. SO_2 , did not give comparable results; the corn was hard to grind and separations were difficult. Poorer results were obtained with HCl . On the other hand steeping with 0.2 per cent. lactic acid produced protein disintegration about equal to that given by a 0.1 per cent. SO_2 steep and a softening action approximating that produced by a 0.2 per cent. SO_2 steep. The addition of lactic acid to SO_2 steeps increased the softening action of the latter. These workers attribute the specific action of SO_2 to its reducing properties rather than to its acidity inasmuch as sulphites exert a dispersing effect on some proteins and reducing agents activate papainases¹³ which may also play a part in the general action.

The principal objections to the use of SO_2 arises from the fact that at the temperature and pH required to secure its beneficial effects, the SO_2 volatilises from aqueous solutions and that these solutions are acid. Its corrosive action is high not only on equipment but also on structural parts of process buildings. The acid tends to modify the starch by a hydrolytic action, which is first noted by a significant loss in potential paste viscosity of the starch.

Accordingly, considerable attention has been given to a study of other steeping agents, particularly those less acidic than SO_2 . Sodium benzoate has been proposed¹⁴ but apparently the addition of some SO_2 in this system is required as well. The use of organic halogen compounds such as monochlorobenzene and o-chlorotoluene have been patented by Berquist.¹⁵ Bartman¹⁶ claimed the use of formaldehyde to be effective and Eckland¹⁷ recommended the use of ozone.

Stratton¹⁸ was among the first to advocate the use of an alkaline steeping medium and the alkaline process described by Kingsford¹⁹ was used for many years until it was abandoned for the more efficient SO_2 process. More recently, Wagner^{20, 21} has again directed attention to the use of caustic alkalis.

Other workers have experimented with steeping technique in order to employ SO_2 to best advantage, that is, to obtain the benefits of this specific steeping agent and to minimise the disadvantages, as noted above. Some of these results will be mentioned in a discussion of steeping methods which follows.

The most elementary method of steeping consists of partially filling a wooden vat, holding about 2,000 to 2,500 bushels of corn, and covering the grain with warm water containing a steeping agent such as SO_2 . The temperature is maintained at about 50° C. for 40 to 48 hours after which the steep liquor is drained from the softened grain which is then sent to the mills.

The principal objection to this method is the relatively large amount of water which is required to soften the grain and to remove a sufficient proportion of water soluble constituents. Modern milling and refining systems are designed to handle steeped grain containing between 3 and 4 per cent. water soluble material ; some require a lower percentage.

This system does, however, possess certain inherent advantages when comparison is made with systems employing counter-current, or diffusion cell principles, designed to obtain a more efficient removal of soluble material for the use of a given quantity of steeping liquor. As pointed out by Kerr²², the single vat system readily permits the addition of germicide at the place where it will be most effective. Both the incoming corn and the process water from the mill house, which is the liquor usually used for steeping, are the principal carriers of micro-organisms into the steeps. Therefore, since both the grain and the process water are exposed to the highest concentration of SO_2 used in this system, it follows that, in order to limit microbiological activity to a given level, a smaller addition of germicide is required in this system than in countercurrent systems wherein the incoming grain is exposed to the lowest SO_2 concentration.

If SO_2 or other hydrolytic agents are used in steeping, then the corn in single vat steeping is subject to lower concentration of acid and consequently the starch may be exposed to less degradative influences. Moreover, the acid activity or H-ion concentration in steeping liquor is not necessarily the same as the pH of the water phase within the grains or the moisture layers adjacent to the starch granules. The H-ion concentration of acids which enter the grain is reduced by the natural buffering systems of the corn such as phosphates and phytin. These buffers are soluble in warm acidulated water and if an excessive proportion of steeping liquor is used, particularly by a system using a counter-current flow principle, the buffers are soon removed. The grain then gradually assumes the pH of the steeping medium. It can be seen that in single vat steeping, conditions are favourable for maintaining a large differential between the pH of the corn and the pH of the steeping medium.

The result of the advantages noted is that starch obtained from corn steeped by the single vat method has a relatively high paste viscosity. Because of the poor economy in the use of water in the single vat system, steeping is now done by methods which employ countercurrent flow. Indeed, the entire mill house, in addition, operates on this principle as well. Fresh water is used in the last stages of washing the refined starch. This water is

then re-used in a preceding phase of starch manufacture, such as flushing the starch from the sedimentation tables. Finally, after having been used in turn in the various operations in the mill house and having attained a content of water soluble material between 400 and 1,000 grains per gallon, the water is run over an absorption tower where the desired amount of SO_2 is taken up and it is then sent to the steeps.

One of the most common forms of countercurrent steeping is the use of about 12 to 14 wooden vats, or open steeps as they are called in practice. These are, in effect, arranged in series. At one end of this series, one steep is filled with dry corn. At the other end, one steep contains corn which has been fully steeped, and this is emptied by running the steeped grain to the mills. To the next steep from this end of the series, that is, the steep which will be the next to supply the mills with corn, fresh steeping liquor is added. When this steep is full, the water may be circulated by pump from the bottom of the steep, through a heating device to maintain the temperature at the desired level and then to the top of the same steep. After a predetermined length of time, the water is removed from all steeps, in turn, and advanced to the next steep in the direction of the one which was last filled with dry corn. After the water has been used on dry corn the liquor is then pumped to evaporators to recover the soluble solids. Obviously, the advancement or change of water in the series of steeps starts by taking water from the steep most recently filled with corn and water, discarding a part of the water as spent steepwater and using the balance to cover partially the corn in a steep into which dry grain has just been placed. Water is then advanced to cover the corn in the steep from whence the spent steepwater was taken and also the steep into which the dry grain was placed. Usually two or more advances of water throughout the system are required in order to fill the last two steeps mentioned. This is because of the removal of water as spent steepwater and because of a depletion of the liquid phase by absorption into the grain particularly in the early stages of steeping. The very large amount of manual labour and supervision required can readily be appreciated. For this reason, the custom oft-times develops of by-passing steeps when water is advanced in order more conveniently to cover the dry corn with sufficient liquor. In this case, full use is not made of all the steeping liquor passing through the system. Another disadvantage of this system is that, since the pumping of steeping liquor from one steep to the next is discontinuous, the grain remains uncovered for a substantial portion of the steeping period. When a volatile steeping agent,

such as SO_2 is used, one of the serious disadvantages of this system is the large loss of steeping agent which occurs during the many pumping operations. Not only are costs increased because of the loss, but also the volatile acid is corrosive to equipment and a physiological irritant to the workers, so that the installation and maintenance of a ventilating system is required.

Some of the mechanical disadvantages of the use of open steeps in series are avoided by employing closed iron steeps, each connected to the next by pipes from the bottom of one to the top of an adjacent steep. Steeping liquor is applied at one end of this system under a hydrostatic head sufficient to cause it to flow through the entire series and void itself at the other end as spent steepwater. Discontinuity of steeping is only momentary and this is when a steep filled with dry grain is connected into the system and when one is disconnected at the other end, drained of steeping liquor and its contents sent to the mills. Full advantage is taken of countercurrent flow in the extraction of soluble material.

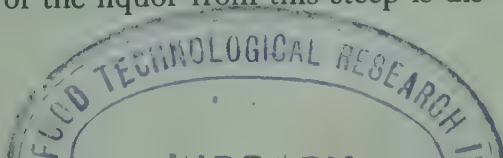
The results achieved in respect to the separation of starch and its quality are, however, approximately the same for the two systems described. In both there is a measurable loss of potential paste viscosity which is attributed to the removal and neutralisation of buffers within the grain and a rapid drop of the pH to a value approximating that of the steeping medium.²² When 10 to 11 gallons of steeping liquor, containing 0.15 per cent. to 0.20 per cent. SO_2 and an acidity of pH 3.5 to 3.8, are added per bushel of corn, and the steeps maintained at 125°F . for 40 to 48 hours, the pH of the grain will be reduced from about 6.4 to about 4.0 and the starch obtained will have a paste viscosity of about 90 by Scott Test. Using corn of normal moisture content, about 5 or 6 gallons of steepwater per bushel of corn is obtained which contains about 6 per cent. of the weight of the grain as soluble and suspended material, has a pH of 4.0 to 4.2 and contains about 0.04 per cent. SO_2 . The steeped corn grain contains about 3 to 3.5 per cent. water soluble material and approximately 45 per cent. moisture. The use of high moisture corn necessitates either the addition of less steeping liquor or the withdrawal of more steepwater, per dry unit weight of corn. The latter procedure is usually employed. Poor separations in milling usually result for several reasons, one of which is an excessive removal of from the corn of ion substances which facilitate the sedimentation of starch from gluten. Considerable thought should be given to adjusting the time and temperature of steeping, the volume and SO_2 content of the steeping liquor to the values which are most suitable with

respect to the physical characteristics of the grain which is to be processed.

The paste consistency of starch within untreated corn grain is probably equal to about 125 by Scott Test, in some instances higher. Starch obtained from corn which has been steeped by the use of the single vat system has a paste consistency of about 115 by Scott Test when a steeping liquor of the same characteristics as described above for countercurrent flow is used and a temperature of 125° F. is maintained for 44 hours. As high as 120 Scott Test may be obtained if the steeping liquor used contains 0.08 to 0.10 per cent. SO_2 , which value appears to be ample for this process.

Several variations in circulating the water or in applying the germicide have been tried in order to retain the principles of countercurrent flow and to eliminate the disadvantages mentioned. In one arrangement, the steeping liquor, after leaving the sulphur tower, is run over a steep of dry corn first and then applied to the end of the series which contains corn steeped the longest time. Three advantages are apparent. The temperature of corn entering the system is raised more quickly; better use is made of the SO_2 employed to inactivate organisms both in the process water used and on the incoming corn; the high peak of SO_2 concentration prevailing in the early stages of countercurrent flow steeping is reduced. In another modification, SO_2 is introduced at several places in the series of steeps. The SO_2 content of the steeping liquor is kept within narrow limits. However, in this procedure, either several additional sulphur towers are required, one for each location where, between the steeps, the SO_2 content of the liquor is to be raised, or else if H_2SO_3 is mixed into the steeping liquor at these several places, the water consumption required for steeping is increased owing to the low strength of acid made by the absorption method.

Another arrangement has been proposed by Kerr²² wherein only three steeps are used in series and the time allotted to the third and last steep is short, about one to two hours. In this last steep, the corn is treated with what amounts to a wash, using gluten overflow water made 0.08 per cent. SO_2 and the corn is then sent to the mills. All of the water from this steep is placed on corn in the second steep for a period of 22 hours. A portion of the water from the second steep is discarded (about 0.8 gallons per bushel) and the balance is sent to the first into which dry corn has been placed. Gluten overflow water from the sulphur tower is used to fill the steep and to raise the SO_2 content of the steeping liquor to 0.12 per cent. All of the liquor from this steep is dis-



carded. This amounts to about 5.5 gallons per bushel of corn of normal moisture content and with the 0.8 gallons discarded from the second steep, a total of about 6.3 gallons of steepwater is obtained. Microbiological activity is very well controlled, for a minimal addition of SO_2 . Steeped corn is obtained containing about 3.75 per cent. water soluble material. The pH of the grain is maintained above 4.5 up to the last washing stage. Starch with a paste viscosity of about 110 by Scott Test is obtained after milling the corn.

IV. Milling and Separation.—After steeping, the corn is passed through several grinding and sieving operations, during which the germs, hulls, fibre, and other constituents are progressively removed and finally only starch and gluten remain.

The corn is passed first through coarse mills. These are frequently called degerminating mills since the primary object at this stage is to crack open the grain and free the germ, preferably without breaking or crushing the latter. Other objects are to loosen the hull and coarsely disintegrate the endosperm. Equipment suitable for this purpose is the Fuss mill which consists of two metal plates, 36 in. in diameter and studded with metal teeth. The plates stand upright in a bronze lined housing. One plate is stationary while the other revolves at about 900 r.p.m.

Process water is added to corn entering the degerminators and additional process water containing starch in suspension is added to the macerated corn in order to form a slurry which can be pumped to the germ separator vats and in order to adjust the density of the slurry to a value at which the germs will float. This value is about 8 to 10.5° Bé. The temperature is 90 to 95° F.

Germ separators are V-shaped vessels about 4 ft. wide, 6 ft. high, and 10 to 15 ft. long. The magma enters at the top at one end. The hulls, and coarse grits tend to settle out as the slurry is propelled to the opposite end of the vat by means of an agitator near the bottom and this heavier material is removed through an opening in the bottom of the vat. The germs tend to float and are taken off the top by overflowing into a weir box at the end of the vat opposite to that at which they entered. Usually a series of paddle wheels or drag sweep paddles aid the movement of the germs across the surface.

The finer particles and liquor are removed from the heavy material leaving the germ separators by passage over copper sieves of the rotating type which are generally referred to as reels. The advantage of rotating reels over shaker sieves for separations of this type are pointed out in the patent to Jeffries.²³ The coarse material which contains the hulls and a small percentage of germs

and coarse grits are passed to a second set of degerminating mills. The grist is combined with the liquors from the reels and, after adjustment to a density of 8 to 10° Bé, the magma is passed to a second set of germ separators.

The germs are collected and washed on a series of reels to remove the adhering starch. The germs are dewatered in squeeze presses and driers and are then treated either in heated expellers or solvent extraction systems to remove the oil they contain.

The degerminated underflow from the separators is passed over a series of reels to recover the liquor and very fine material which, after passage over silk sieves, may be returned, in part, into another cycle of the germ separating process, or it may pass on to the system supplying the starch tables or centrifuges. The coarse grist which contains hulls, fibre, and particles of the endosperm are finely ground in stone mills. These are usually buhrstone mills and consist of a furrowed grinding stone, revolving at high speed above a similar stationary stone. The object is to produce a high degree of disintegration in order to free the starch granules so that they may now be separated from the hulls and fibre in the sieving and washing operations which follow. In this process, the glutinous portion of the endosperm becomes very finely divided as well, so that, when the hulls and fibre are removed by passage over reels and shakers, a slurry of starch and gluten remains. The coarse material from the buhr mills is removed and washed on a series of reels after which the fine fibrous material is removed on silk shaker sieves. The presence of relatively small amounts of fibre interferes with the separation of the starch from gluten in the sedimenting or centrifuging operations.

The slurry of starch and gluten is now adjusted to the desired density for separation of the starch. Even though a counter-current principle is used in washing the adhering starch from the various grists, the recovered solids usually do not increase the density of the liquors to the value desired in some systems for tabling or centrifuging the starch. In such cases, the liquors are partially dewatered by passage over Feinc or string filters. These are continuous, revolving drum, suction filters resembling a large Oliver Filter but equipped with a series of strings which pass around the drum and thence to a roller at some distance so that the layer of filter cake is readily lifted from the drum by the strings.

The most elementary method for separating starch from dispersed gluten is to run the mill liquor into a vat, allow the starch to settle for several hours and then draw off the supernatant liquor which contains a large share of the gluten. More gluten may be

washed from the surface of the starch by the use of a jet of water and gentle agitation. Resuspension of the settled starch is accomplished by adding fresh water and using wooden, sweep agitators which are attached by drag chains to a collar around a central shaft in the vat so that the agitator blades may float and remain free of the settled starch. The efficiency obtained in separating starch from protein by this method is poor.

A second method of separation is to introduce the slurry of starch and gluten continuously into the top of a cone-shaped vat and to draw off the starch as a concentrated slurry at the bottom. Separation of starch from protein is not as complete as is demanded by present-day standards. However, the general principle of a continuous gravity separator is sound and the application deserves further study, taking advantage of progress that has been made in the development of continuous separators or concentrators in other industries.

The principles of flotation which have been developed and applied with considerable success in recent years, particularly in the purification of ores, has been applied to the separation of starch from gluten. By the use of selected frothing agents and depressants, either the gluten or the starch may be floated. At least one large mill in the United States employed this method commercially in the past. However, knowledge of the principles employed were then in a preliminary state of development and present-day, efficient, flotation agents were not available. The process was abandoned many years ago and tables were installed. Several patents²⁴⁻²⁹ have been issued which illustrate the application of flotation to the separation of starch.

Sedimentation of starch from gluten by allowing the liquor to flow continuously along an inclined trough or table, as it is called, is now almost universally employed to make the separation. The dimensions of the table, the inclination used, the rate of flow employed and the results obtained are, to a large extent, determined by the characteristics of the slurry of starch and gluten employed. An important feature is the density. In the early days rather dilute suspensions were used corresponding to about 3° Bé. This value was raised to 6° Bé when the industry 'bottled up' the wet milling process, that is, re-used all process waters either in the same or another cycle of operations and discarded no liquors to the sewer. However, the use of liquors for tabling having a density even as high as 6° Bé requires the handling of about 30 gallons of water per bushel of corn milled in the mill and table house. Since, of this 30 gallons, only about 10 gallons may be passed on to the steep house, such a process requires the re-use

of about 20 gallons of liquid for each bushel of corn processed. (See Table IX, p. 61.)

Obviously, this re-use of liquors, which contain substantial quantities of water soluble and fermentable corn solids, makes more difficult the production of starch, gluten and other products of high quality free from the split-products of degradative reactions caused by organisms or enzymes. A discussion of some of the problems involved in the re-use and re-cycling of process waters will be found in patents issued to Widmer,³⁰ McCoy^{31, 32} McCoy and Sjostrom,³³ Moffett,³⁴ Greenfield,³⁵ Jeffries,³⁶⁻³⁹ and King and Baker.⁴⁰

Considerable study of the use of suspensions of starch and gluten at a higher density has been made in order to eliminate, as far as possible, the re-use of process water in the mill and table house. If densities corresponding to 12 to 13° Bé are employed, only 10 to 12 gallons of liquor per bushel of corn are needed in the mill house and most of this liquor may be passed on to the steeps.⁴¹ All other conditions equal, the lower the density used, the more easily is starch sedimented from gluten. In order to maintain a high degree of purity and high yield of starch, or to increase these values as the industry has raised its standards and, at the same time, to increase the density used for separations required a careful study and adjustment of other variables of the process. Kerr⁴² has pointed out the influence of several important ones which are: (a) physical state of the gluten, (b) pH of the slurry, (c) ionic strength of the liquid, (d) temperature of the slurry, (e) the rate of flow of the liquors delivered to the table head, and (f) the characteristics of the table, such as, ratio of width to length, smoothness of the table bed and elevation per unit of length.

The desired physical state of the gluten is attained by proper steeping and milling. A satisfactory range of acidity for tabling is between pH 3.8 and 4.2. Separations become more difficult if the pH is displaced outside of this range, e.g. pH 3.0 or pH 5.0. A total concentration of the electrolytes common to mill liquors corresponding to about 50 to 150 grains of ash per gallon of liquid appears to be sufficient. If the value is less than this, the starch, particularly the smallest granules, has a reduced sedimentation rate, so that at certain rates of flow on the tables this part of the starch passes off with the gluten. If the rate of flow is reduced sufficiently so as to recover the starch, then gluten will sediment on the table to an unpermissible extent. Highly ionised acids or bases are able to increase the sedimentation rate of starch, an effect observed for potato starch by Wiegel.^{43,44} Therefore, at a very

low pH , e.g. 1.5, or at high pH , such as 10 to 11, starch may be tabled because the favourable influence of increased ionic strength contributed by the acid or base counter-balances the adverse effect of a change of pH away from the optimum range. Within operating limits (75-110° F.), the higher the temperature, the greater is the efficiency of table separation since an increase in temperature reduces the apparent density of the table liquor.

Obviously, if a slurry of starch and gluten is passed over a table at too fast a rate, some starch will pass with the gluten fraction and if the rate is too slow, gluten will sediment with starch. The range of rates of flow at which starch is obtained at the highest purity and yield is very narrow and must be determined for each set of operating conditions. Obviously, the rate should be maintained at the optimal value by automatically controlled devices for delivering the mill starch to the table head.^{45,46}

The rate at which the mill starch moves down a table in unit volumes per unit of table length per minute is determined by the delivery at the table head in unit volumes per minute, the pitch or elevation of the bed and other characteristics of the bed, such as its width. If the width is relatively large compared to the delivery rate, so as to permit a zig-zag course, then the time required for a given volume of liquor to move from one end of the table to the other may be considerably more than anticipated. For an elevation of 1/16 in. per ft., table width should not exceed 1 ft. for each gallon per minute of 12° Bé mill starch delivered to the table head. Unfortunately, the actual pitch of the bed over which the table liquors run does not remain constant during the 3 to 4 hour period normally employed for sedimenting the starch. The reason is that most of the starch in the liquors sediments on the first third of the table's length. Therefore, starch is allowed to accumulate on the table until the speed with which a unit volume of liquor flows down the table becomes such that the recovery of starch falls below an allowable level.

A table length of 120 ft. will be found sufficient for one which is 2 ft. wide and onto which starch liquor of 12° Bé is delivered at a rate of 2 gallons per minute. After the desired amount of starch has been deposited on the table, the flow of mill liquor is stopped, a period for draining is given and the last of the gluten is flushed from the surface of the starch with a small water hose. Frequently a squeegee is employed to facilitate this operation and for this reason the mixture of gluten and the rather appreciable quantity of starch which is removed at this stage is often referred to as squeegee starch.

Finally, the starch is removed by the flow of water from rather

large jets of water under a high pressure.⁴⁷ The water used is from the filters to which the flushed starch is now passed for dewatering.

Several types of filters are used for dewatering and washing the starch. The American Filter is most commonly employed. This consists, essentially, of a hollow disc covered with canvas. The disc is divided into sections so that suction may be applied to sections as they revolve and pass through the filter bed and while wash water is applied to the filter cake by means of sprays. Pressure is applied to sections when the starch is being removed by means of a scraper. The Oliver Filter and other types of drum filters, such as the Feinc Filter, are also used. The Sweetland Filter press is employed occasionally. Centrifuges are also employed for washing and dewatering the starch.

Filtration is facilitated by heating the slurry to about 130° F. and the spray water used to wash the starch on the filter may be 135-140° F. In general, starch in a slightly acidic state, e.g. pH 4.0, filters more rapidly than when the pH is in a higher range. The correct range is normally maintained by the addition of a small amount of SO₂ at the first washing filter. The SO₂, which also serves the purpose of protecting the starch from bacterial contamination during drying, is driven off when the starch is heated in the driers. Filters reduce the water content of starch to about 45 per cent. ; high speed centrifuges reduce the moisture content to 33-35 per cent.

The gluten fraction from the tables is passed to sedimentation tanks, called settlers, or to other suitable concentrating devices. The overflow water from the gluten is used for steeping.

Other systems used industrially for the separation of starch involve the use of centrifuges. Centrifugal separation of starch was proposed in a patent issued to DeCastro and Muller.⁴⁸ Kerr⁴⁹ and Schrader⁵⁰ developed the method and Peltzer⁵¹⁻⁵⁶ and Boie⁵⁷ devised equipment which appears to be particularly adapted to the centrifugal separation of corn starch from corn gluten. In the system described by Peltzer, a slurry having a comparatively high density, e.g. 12° Bé, is delivered continuously to the rotor from whence a substantial portion of the underflow of starch, plus additional liquor, is continuously returned to the centrifugal chamber in order to assist in carrying out the centrifugally separated starch particles. Several centrifuges of this type, frequently referred to as Merco Centrifuges, may be used in series. That is, the underflow of starch may be further refined in a second centrifuge and the overflow of gluten may be treated in a third centrifuge in order to recover additional quantities of

starch. The latter is composed of relatively small starch granules and contains from about 1 to 10 per cent. protein. It is similar in composition to the squeegee starch mentioned above. Other types of centrifuges have been employed, as for example, the continuous DeLaval centrifuge and the intermittently fed, basket type. A novel milling system involving the use of centrifuges has recently been proposed by Peltzer.⁵⁸ In this, fibre and fine grits are not removed from the grist obtained from the buhr mills, but rather, the mill liquors pass to a series of centrifuges. A large share of the fibre passes with the overflow which contains, primarily, the gluten fraction; the remainder of the fine grits is removed from the starch by passage of the centrifuged starch over silk sieves before filtration. One of the principal advantages claimed for this system is a material reduction in the content of water soluble material in the process liquors in the mill houses. A filter is interposed between the mills and the centrifuges and the primary filtrate passes directly to the steepers. The wash water used on this filter is used in the milling operations. The filter cake is repulped to form a slurry of suitable density for use in the centrifuges, using in part, the overflow water from the first centrifuge. The starch fraction receives a wash in the centrifuge by feeding in water obtained from washing the starch on the final dewatering filters. The primary filtrate obtained from the final dewatering filters is used both to wash the grits on the silk sieves which follow the centrifuges and to repulp the mill starch for preparing the feed to the centrifuges. A gluten slurry is obtained of sufficient density so that it may be passed directly to filter presses without the use of gluten setters or other equipment for concentration.

The patents issued to Kelling describe the use of centrifugal separation in modern mill practice.⁵⁹⁻⁶⁵ Centrifuges may be used in combination with tables. Staley⁶⁶ has patented a process, wherein table separation is followed by centrifugation. Many mills now employ continuous centrifuges in order to recover additional starch from the gluten as it leaves the tables and in order to obtain gluten containing a relatively high protein content. By these methods gluten containing 60 to 70 per cent. protein and starch containing as low as 0.2 per cent. protein are commonly obtained in practice.

The secondary starch, containing the smallest starch granules, may be refined by several procedures investigated by the writer. The starch mixture may be made into a dilute slurry with water and the gluten removed by passage through continuous gravity separators; the protein sediments and the starch, containing

about 1 per cent. or less of protein, passes out with the effluent liquors.

Water enters the wet milling system, principally, as moisture in the corn used and as the wash water on the last filter for the starch as it leaves the system. In mills where the starch is converted to sugars, the water used is either softened water or the condensate from various evaporators and boilers. If water is used which contains lime, then the products may be contaminated with gypsum wherever $[Ca] [SO_4]$ exceeds the solubility product constant for this salt. The sulphate ion forms unavoidably by the oxidation of the SO_2 which is commonly added at various places in the system, e.g. at the first starch washing filters, at the table heads, at the grit reels and at the steepers. The water travels in a general countercurrent direction through the table and mill houses and emerges finally as steepwater. The steepwater is evaporated in order to recover the valuable nutritional elements which it contains, such as soluble protein, phosphate, phytate, inositol, and growth adjuncts and in some cases for the production of industrial chemicals, as by-products of the process. A large proportion of the by-products of the wet milling process, such as gluten, the germ cake from the oil expellers, the grits, and steepwater is mixed together in dietetically correct proportions and the product is sold as feed for cattle.

The evaporation of steepwater has presented a problem to the industry in the past because of the heat coagulable material which it contains. The problem has been discussed by Kerr,⁶⁷ who has offered a practical solution to this phase of the problem. Other methods for treating steepwater prior to or during evaporation have been proposed by Jurgensen⁶⁸ and by Schopmeyer.⁶⁹

V. Dehydration.—After washing and dewatering, the starch may be passed on to various processes applied to modify it, or to converters where the starch is hydrolysed to make syrups or sugars, or the starch may be dried directly as unmodified corn starch. Formerly, kilns⁷⁰ were used almost exclusively for the drying operation. In this, the starch cake is broken up and placed in wagons, such as, the Bauer wagon⁷¹⁻⁷² or on trays which are then loaded onto a carrier, and these are moved through a heated tunnel or kiln over a period of from 10 to 20 hours. In the Bauer wagon, the sections stand in a vertical position in contrast to trays which are placed on carriers in a horizontal position. Rotary driers are used, particularly for the rapid and continuous drying of modified starches. The Huhn drier is used for reducing the moisture content from normal levels of 10 to 12 per cent., such as is obtained in kiln drying, to 5 to 7 per cent. The latter

operation is employed, for example, prior to dextrinisation of starch.

Modern practice makes use of continuous belt driers, such as for example, one manufactured by Proctor and Schwartz. In the final filtration, the starch is accumulated on a revolving drum of the Oliver type, so as to form a sheet 0.25 to 0.50 in. thick. The sheet is scored so as to break into ribbons about 1 in. wide.⁷³ These ribbons fall onto breakers which form lengths of about 2 in. These sections of filter cake, which are relatively uniform

TABLE VIII

Effect of Steeping Adjuncts on Corn at 49° C.

<i>Steeping Medium</i>	<i>Steeping Time</i>	<i>Condition of Protein Matrix</i>	<i>Yield of Starch, %</i>
Distilled H ₂ O	4	Coarse, holding starch tightly	—
	24	Slightly less coarse, but holding starch tightly	64
0.1% SO ₂	4	Slightly less coarse than unsteeped corn but holding starch tightly	—
"	24	Somewhat less coarse but holding starch tightly	82
0.2% SO ₂	8	More dispersed than after 24 hrs. steep in 0.1% SO ₂	—
	24	Not appreciably different from 8 hrs.	83
0.3% SO ₂	4	Much dispersed	—
"	24	In separate particles, no network remaining	88
0.4% SO ₂	4	Indistinguishable from 4 hr. steep in 0.3% SO ₂	—
"	24	Indistinguishable from 4 hr. sample	89
*Acetic Acid	24	Hard to grind, poor separation of starch	70
*HCl	24	Easy to grind, but poor yield due to large gluten particles	56
0.1% Lactic Acid	24	Softening about equal to a 0.1% SO ₂ steep	—
0.2% " "	24	Softening about equal to a 0.2% SO ₂ steep; protein disintegration about equal to 0.1% SO ₂	—

* Equivalent concentration to 0.2% SO₂.

in size, are deposited onto an endless belt made of bronze wire, which carries the starch through a tunnel or series of heated chambers during a period of from 30 to 45 minutes. Heated air is blown through the bed of starch, which is about 1.5 to 2.5 in. in depth. The temperature employed, the speed of the belt, and the depth of starch on the belt are mutually interdependent variables. These are adjusted so as to obtain the final desired moisture content for the volume of starch which it is desired to pass through the drier per unit time. The air temperature in these driers varies from about 120° up to about 285° F. In the last section a forced draft of cold air is applied in order to cool the starch. This procedure has certain advantages over older

methods of drying, all of which result in obtaining a starch degraded to a minimum extent in the final operation. A reduction in drying time to less than one hour very nearly obviates the necessity for adding SO_2 to the starch wash water in order to protect it from bacteriological contamination during a long drying period. A reduction in the acidity of the starch and a reduction in the time the acidified starch is exposed to higher temperatures, reduces the loss in paste viscosity normally experienced in kiln

TABLE IX

Relationship of Baume to Dry Substance for Starch Suspensions at 60° F.

Degrees Baume	(Air) Specific Gravity	Per cent. D.S.	Grams D.S./100 ml.	Pounds Per gal.	Pounds D.S./Gal.
0.00	1.0000	0.00	0.00	8.328	0.000
1.00	1.0069	1.78	1.79	8.386	0.149
2.00	1.0140	3.55	3.60	8.445	0.300
3.00	1.0211	5.33	5.44	8.504	0.453
4.00	1.0285	7.11	7.31	8.565	0.609
5.00	1.0358	8.89	9.21	8.626	0.767
6.00	1.0433	10.66	11.12	8.689	0.926
7.00	1.0508	12.44	13.07	8.751	1.089
8.00	1.0585	14.22	15.05	8.815	1.253
9.00	1.0663	15.99	17.05	8.880	1.420
10.00	1.0742	17.77	19.09	8.946	1.590
11.00	1.0822	19.55	21.16	9.013	1.762
12.00	1.0903	21.32	23.25	9.081	1.936
13.00	1.0986	23.10	25.38	9.150	2.114
14.00	1.1071	24.88	27.54	9.220	2.294
15.00	1.1156	26.66	29.74	9.291	2.477
16.00	1.1242	28.43	31.96	9.362	2.662
17.00	1.1330	30.21	34.23	9.436	2.851
18.00	1.1419	31.99	36.53	9.510	3.042
19.00	1.1510	33.76	38.86	9.586	3.236
20.00	1.1602	35.54	41.23	9.662	3.434
21.00	1.1696	37.32	43.65	9.741	3.635
22.00	1.1791	39.09	46.09	9.820	3.839
23.00	1.1888	40.87	48.59	9.900	4.046
24.00	1.1986	42.65	51.12	9.982	4.257
25.00	1.2086	44.43	53.70	10.065	4.472

drying. Local overheating of the starch is much less when the endless belt type of drier is used than when kilns or rotary driers are used. Very frequently starch is found in some sections of the wagons emerging from kilns having as little as 2 per cent. moisture content while in other sections the starch will contain 18 to 200 per cent. moisture.

Starch from the driers is crushed to a pearl form or it is milled, as; for example, by the use of rollers as in the Pope Mill, then bolted through silk sieves in order to obtain a powdered form.

The lump varieties of starch, the so-called crystal forms, are made by two general methods. A slurry of starch is dewatered either by gravity or suction in a box type of filter lined with canvas. The cubes are placed in crusting kilns during which treatment the starch partially dries. Thereafter, the crust is removed and discarded; the core of the cube is dried to normal moisture levels and then broken into the desired particle size. An alternate method has been patented by Moffatt.⁷⁴ Moist starch is pressed so as to form a cake by the use of a heated cylinder provided with a piston for applying pressure. The cake is allowed to age and is then dried to a normal moisture level after which it is broken into the desired particle size.

REFERENCES

1. T. KINGSFORD, 'The Starch Industry', *One Hundred Years of American Commerce*, edited by C. M. DEPEW, New York, 1895, Chapter 48, p. 457.
2. *U.S. Tariff Comm. Rept.* 138 (1940).
3. J. H. SCHOLLENBERGER and C. M. JAEGER, 'Corn, Its Products and Uses,' U.S. Dept. Agr., Bur. Agri., and Ind. Chem., *ACE* **121**, p. 1-47 (1943).
4. A. S. HITCHCOCK, *Manual of the Grasses of the U.S.*, Washington D.C., 1935.
5. F. W. BARTLING, *American Miller*, December, 1939, p. 26.
6. F. W. BARTLING, *American Miller*, February, 1940, p. 24.
7. E. B. EARLY and E. E. DE TURK, *J. Am. Soc. Agron.*, **36**, 803, 1944.
8. R. W. KERR, *Chemistry and Industry of Starch*, New York, p. 85, 1944.
9. M. J. COX, M. M. MACMASTERS, and G. E. HILBERT, *Cereal Chem.*, **21**, 447, 1944.
10. F. W. BARTLING, *American Miller*, April, 1940, p. 24.
11. J. E. KILLINGER, *Dissertation*, Iowa State College, Iowa, 1938.
12. F. FEIGEL, *Z. Anorg. Allgem. Chem.*, **203**, 57, 1931.
13. H. S. OLCOTT, L. A. SAPIRSTEIN and M. J. BLISH, *Cereal Chem.*, **20**, 87, 1943.
14. W. F. HENRY and J. P. BISHOP, U.S.P. 2,322,413, 1943.
15. C. BERQUIST, U.S.P. 2,228,717, 1941.
16. L. BARTMAN, U.S.P. 1,670,015, 1928.
17. E. ECKLAND, U.S.P. 1,000,726, 1911.
18. S. T. STRATTON, U.S.P. 22,460, 1858.
19. T. KINGSFORD, U.S.P. 280,044, 1883.
20. T. B. WAGNER, U.S.P. 2,192,212, 1940.
21. T. B. WAGNER, U.S.P. 2,284,239, 1942.
22. R. W. KERR, *Chemistry and Industry of Starch*, New York, p. 20, 1944.
23. L. F. JEFFRIES, U.S.P. 1,007,784-5, 1911.
24. J. L. BERRIGAN, U.S.P. 994,497, 1911.
25. H. C. HOLDEN, U.S.P. 1,221,990, 1917.
26. R. G. BRINDLE, B.P. 159,838, 1922.
27. A. PELTZER, U.S.P. 2,039,605, 1936.
28. T. B. WAGNER, U.S.P. 2,132,251, 1938.
29. F. O. GIESECKE, U.S.P. 2,251,448, 1941.
30. J. M. WIDMER, U.S.P. 1,585,452, 1926.
31. R. MCCOY, U.S.P. 1,651,611, 1927.
32. R. MCCOY, U.S.P. 1,832,229, 1931.
33. R. MCCOY and O. SJOSTROM, U.S.P. 1,828,334, 1931.
34. G. M. MOFFETT, U.S.P. 1,655,395, 1928.

35. R. E. GREENFIELD, U.S.P. 2,023,999, 1935.
36. F. L. JEFFRIES, U.S.P. 2,050,330, 1936.
37. F. L. JEFFRIES, U.S.P. 2,065,313, 1936.
38. F. L. JEFFRIES, U.S.P. 2,088,706, 1937.
39. F. L. JEFFRIES, U.S.P. 2,122,647, 1938.
40. P. KING and R. D. BAKER, U.S.P. 2,237,561, 1941.
41. A. PULFREY, R. W. KERR, and H. R. REINTJES, *Ind. Eng. Chem.*, 1940, **32**, 1483.
42. R. W. KERR, *Chemistry and Industry of Starch*, p. 34, Academic Press, Inc., New York, 1944.
43. E. WIEGL and H. SCHÜLER, *Kolloid—Z.*, 1935, **71**, 65.
44. E. WIEGL, *Zeit. Spiritusind.*, 1935, **58**, 205.
45. H. W. CURRY, U.S.P. 1,977,792, 1934.
46. S. SHURBOCK, U.S.P. 2,066,142, 1936.
47. A. W. H. LENDERS, U.S.P. 1,456,243, 1923.
48. J. DeCASTRO and T. H. MULLER, U.S.P. 273,128, 1883.
49. G. A. KERR, U.S.P. 471,614, 1892.
50. R. SCHRADER, U.S.P. 757,778, 1904.
51. A. PELTZER and A. PELTZER, Jr., U.S.P. 1,923,454, 1933.
52. A. PELTZER and A. PELTZER, Jr., U.S.P. 1,923,455, 1933.
53. A. PELTZER and A. PELTZER, Jr., U.S.P. 1,933,119, 1933.
54. A. PELTZER and A. PELTZER, Jr., U.S.P. 1,945,786, 1934.
55. A. PELTZER and A. PELTZER, Jr., U.S.P. 2,013,668, 1935.
56. A. PELTZER, U.S.P. 2,097,531, 1937.
57. H. BOIE, U.S.P. 2,124,284, 1938.
58. A. PELTZER, U.S.P. 2,316,807, 1943.
59. A. H. KELLING, U.S.P. 2,100,744, 1937.
60. A. H. KELLING, U.S.P. 2,103,217, 1938.
61. A. H. KELLING, U.S.P. 2,114,497, 1938.
62. A. H. KELLING, U.S.P. 2,115,170, 1938.
63. A. H. KELLING, U.S.P. 2,115,171, 1938.
64. A. H. KELLING, U.S.P. 2,124,779, 1938.
65. A. H. KELLING, U.S.P. 2,133,543, 1938.
66. A. E. STALEY, U.S.P. 2,116,610, 1938.
67. R. W. KERR and H. BERLIN, U.S.P. 1,918,812, 1934.
68. R. P. JURGENSEN, U.S.P. 2,298,623, 1942.
69. H. H. SCHOPMEYER, U.S.P. 2,302,393, 1942.
70. J. J. MERRILL, U.S.P. 1,183,097, 1916.
71. L. P. BAUER, U.S.P. 1,035,302, 1912.
72. L. P. BAUER, U.S.P. 1,061,720, 1913.
73. L. P. TIERS, U.S.P. 2,327,943, 1943.
74. A. U. MOFFATT, U.S.P. 541,125, 1895. U.S.P. 541,941, 1895.

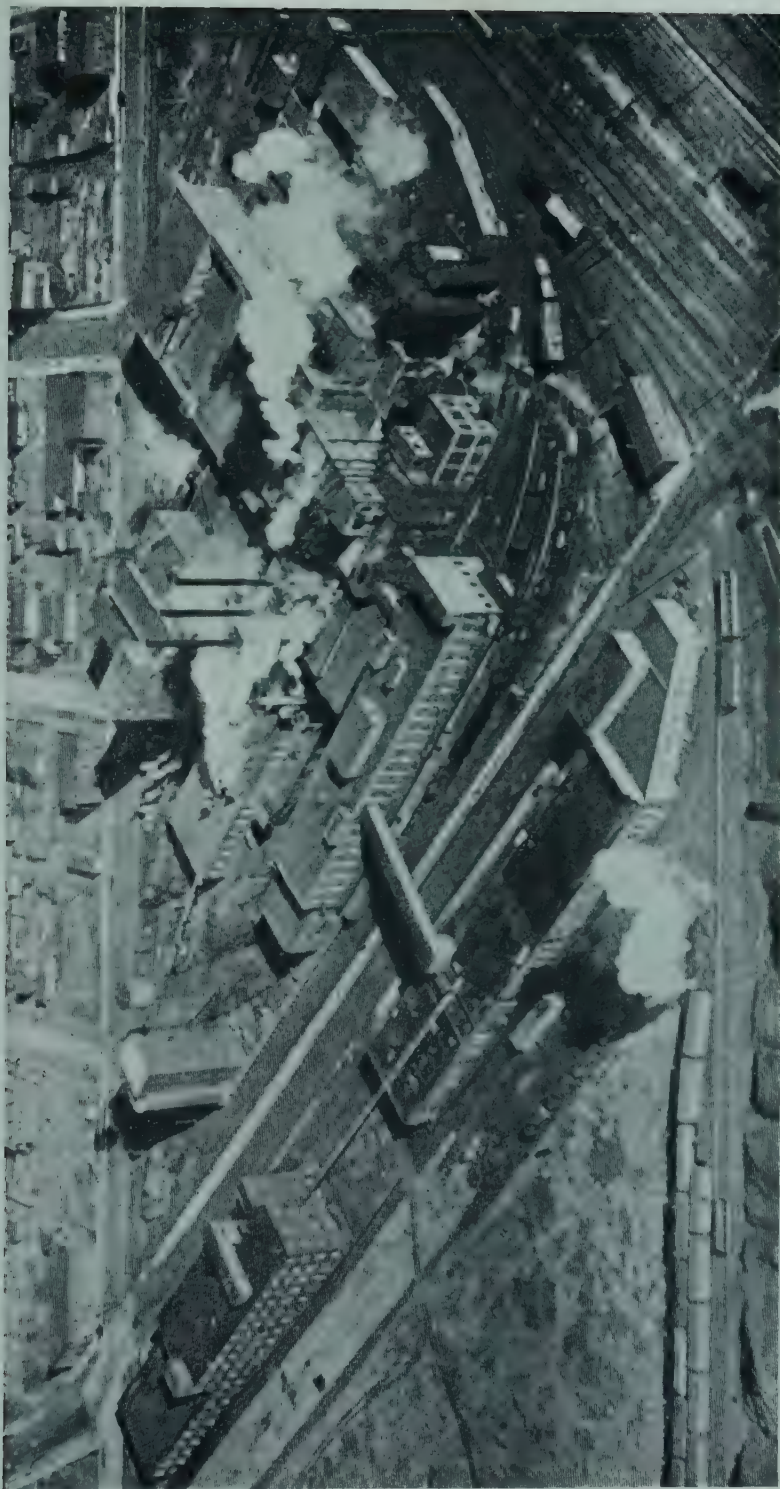
CHAPTER 4

GLUCOSE AND MALTOSE

The Manufacture of Glucose.—Kirchhoff discovered, in 1811, that heating starch with dilute sulphuric acid transformed it into sugar, although his object had been to prepare a light-coloured substitute for gum arabic. As the English were blockading France at that time, the importance of the discovery was quickly realised and manufacturing operations began at once. It was thought at first that the sugar obtained was identical with cane sugar, and could be substituted for it in any product, but later it was found to be less soluble and less sweet, and, as it could not be used in every case as a substitute for sugar, it fell into disrepute for a long time. When the blockade was lifted, production of starch sugar fell off greatly, owing to the heavy fall in price consequent to the market being flooded with colonial products, and to the strong competition of beet sugar. It had, however, gained a foothold in the brewing industry and for the manufacture of spirituous liquors. That starch sugar is identical with grape sugar was established by Saussure¹ in 1814, and he correctly explained the mechanism of the process as one of hydrolysis.

Commercial dextrose is marketed in three forms: (a) starch syrup, glucose syrup or corn syrup, (b) glucose, (c) commercial dextrose. The first is a thick, pale or colourless syrup containing from 12-20 per cent. moisture and colloidal matter like dextrin, which prevents crystallisation taking place. The solid glucose appears as pale to brown-coloured amorphous masses, although in reality it is made up of minute crystals. The colour and amount of dextrose are determined by the method of manufacture, and the terms '70' or '80' sugar are used to denote the percentage content of dextrose. Commercial dextrose is a fine crystalline powder containing from 80 to 99.5 per cent. of pure sugar, according to the conditions of crystallisation. One refined brand, known as 'Cerelese',² contains 1 molecule of water of crystallisation, has an average sugar-content of 91.4 per cent., and ash-content 0.05 per cent.

W. B. Newkirk³⁵⁻³⁷ has described in some detail the preparation of anhydrous glucose and dextrose hydrate and his work is discussed below.



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FIG. 4:1. Illinois plant of Union Starch and Refining Company. Aerial view showing layout.

[Facing p. 64.

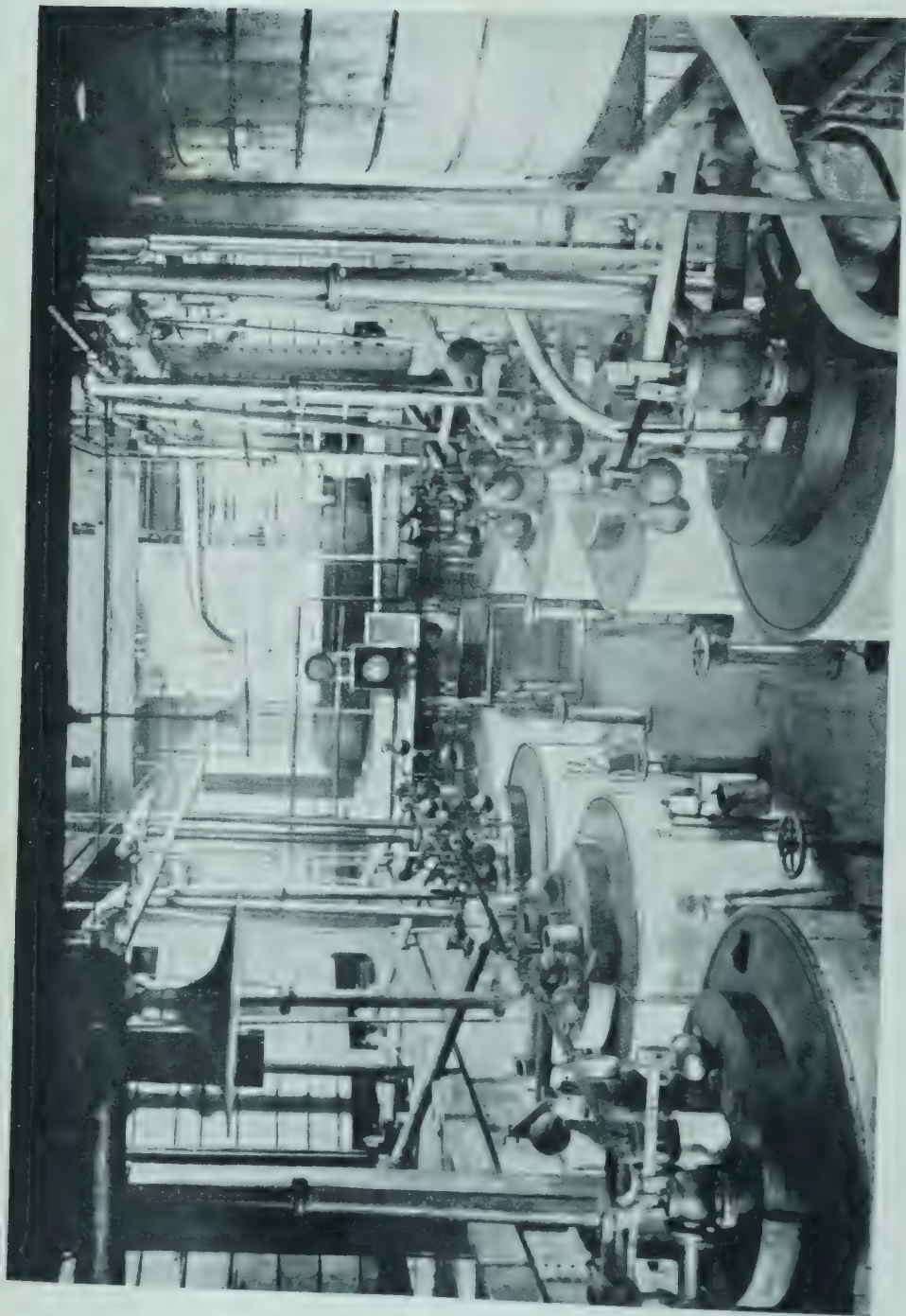


FIG. 4:2. Converter floor where starch is converted to sugar liquor. [Reproduced by courtesy of 'Industrial and Engineering Chemistry']

Starch syrup for confectionery should contain as little acid as possible, otherwise during 'boiling' in confectionery manufacture the sucrose used in conjunction with it will be inverted. On the other hand, W. Ekhard³ points out that some acidity is required, otherwise a yellow colour develops during the 'boiling'. This acidity, which is due to acid phosphates, should not fall below 0.3 per cent. if the yellowing is to be avoided. For these reasons Preuss⁴ considers that sodium carbonate should be used to neutralise the hydrochloric acid used in the conversion, as the salt formed is without hydrolytic action on sucrose and, in the concentration as left in the syrup, does not affect the flavour; whereas if chalk is used, the resultant calcium chloride would have a strong inverting action when used in confectionery. If sulphuric acid has been used to hydrolyse the starch, chalk may be used, as the resulting calcium sulphate can be readily removed.

The amounts of oil and protein in the syrup are other factors determining its value for confectionary processes; when these exceed 0.14 and 0.19 per cent. respectively,⁵ they cause darkening when the syrup is heated to 145° C. Potato starch, being freer from protein matter than maize starch, gives syrups that are superior in this respect.

Raw Materials.—The amylaceous matter used is generally 'green' starch, from maize, wheat, rice, or potatoes, and is often produced at the factory, especially maize starch. The grains of the cereal may be used, but then a less pure product may result, although rice with its high starch-content lends itself perhaps more readily to this treatment than the other cereals. L. E. Stout and C. G. Ryberg³⁰ have suggested the use of sweet-potato starch as a starting material and have determined the effect of pressure and of acid concentration on the rate of hydrolysis. The isoelectric point of the undesirable humus was found to lie at pH 5.1 and the conditions for decolorising the syrup were determined. The results show that sweet-potato starch does not differ very much from maize starch in its ease of conversion or the conditions it requires and that a product comparable in flavour and appearance can be produced. Highly modified soluble starch has been used by C. B. Duryea.⁶

The acids generally favoured are sulphuric acid in Europe and hydrochloric acid in America. Other acids have been proposed from time to time, including nitric,⁷ hydrofluoric⁸ and phosphoric⁹ acids, but these have not found much favour. Of these acids it will be noticed that the last two could be readily removed by chalk, but this advantage does not appear to have outweighed the disadvantage of higher cost.

Earlier Process.—In making glucose by the earlier processes sulphuric acid is employed, to the extent of about 0.05-1.25 per cent., to hydrolyse the starch, which is suspended in 2-2½ times its weight of water contained in wooden vats provided with a steam coil. Water and acid are first heated to boiling-point and the starch-milk run in. If 'green' starch is used, allowance is made for the moisture in it (45-55 per cent.); for the production of solid sugar the higher figure for acid is employed. During the boiling which follows the addition of the starch-milk, volatile odoriferous substances are driven off, especially when potato starch is used (see p. 10), and, in that case, it is preferable to boil for a longer time, so that the characteristic odour may be completely expelled.

The course of the conversion is followed in the first stages by means of the iodine reaction, which indicates the point at which the transformation of the starch into glucose and lower dextrins is complete. From this point the hydrolysis of the residual dextrins is followed by withdrawing samples of the syrup and adding double the volume of alcohol, when these compounds are precipitated. The liquor is neutralised when this test gives no precipitate.

As lime would react with the glucose, chalk is used as the neutralising agent, and when nearly neutral the liquid is again boiled for a short time before the final addition of chalk. Although at this point no precipitate is obtained in the alcohol test, yet some substance other than glucose is present which is not precipitated by alcohol at that concentration, and it appears in the final glucose, unless boiling is continued for a further short time.

The calcium sulphate is allowed to settle, or filtered through a filter press, and the liquor is evaporated until more calcium sulphate separates, when it is again filtered and evaporated in vacuum pans to a thick syrup. If a good coloured, solid sugar is required, the syrup is filtered through animal charcoal before the last evaporation, and the final syrup soon begins to crystallise.

The above process may be carried out under pressure if desired, and with the proportions mentioned above, the temperature should not exceed 130° C.; also, the time of heating should be carefully controlled, otherwise the sugar decomposes and gives a lower yield of an inferior product.¹¹ If the process is carefully carried out glucose of 92-97 per cent. purity is obtained. E. Parow⁵ has shown that with potato starch increase of pressure leads to a rapid increase in the rate of hydrolysis, but, as previously indicated, it is preferable to operate at the moderate pressure for

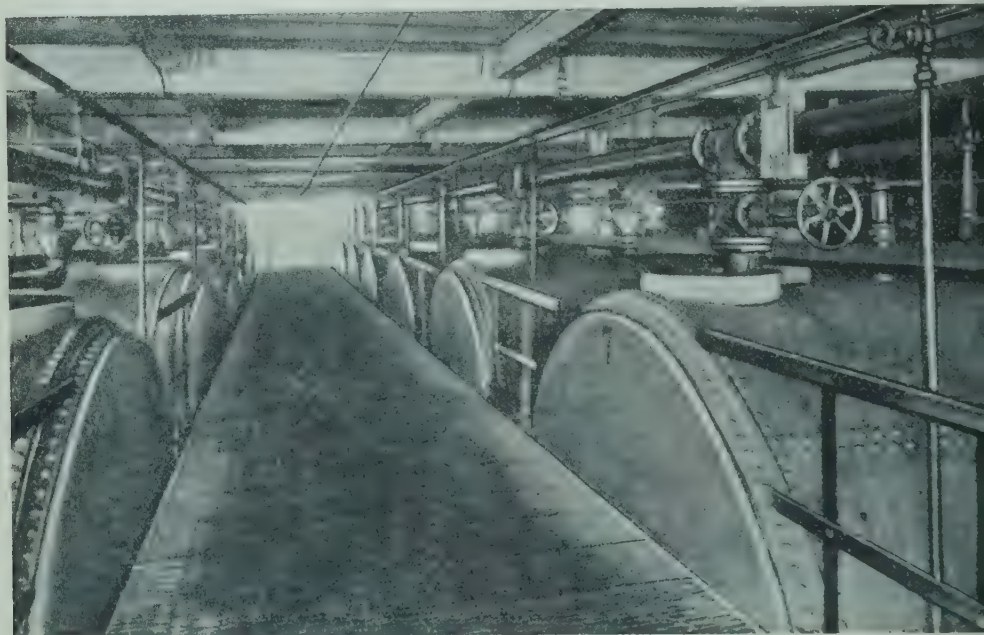
a longer time in order to expel the characteristic smell of potatoes from this starch. The more recent process uses pressure.

The More Recent Process.—In this process, which in the United States is used almost exclusively, water containing 0.12 per cent. of hydrochloric acid on the weight of starch to be processed is heated to the conversion temperature in cylindrical copper vessels, which may be as much as 20 ft. high and 6 ft. in diameter, and the starch suspended in cold water is pumped in. The process of charging may take from 15 to 20 minutes, and the continual influx of new material prevents the formation of gelatinous lumps; after the addition is finished, a few more minutes suffice to complete the conversion. The temperature throughout the entire operation is maintained between 132° and 137° C. If solid glucose is being prepared, the acid may be increased to 0.2 per cent. on the weight of starch present, to give a liquid of 10° Bé., and higher temperatures and pressures may be used. When some dextrin is still present, as shown by the iodine and alcohol tests, which may occur after some 5-7 minutes' heating following the final addition of starch-milk, the conversion is stopped by releasing the pressure. The process is interrupted at this point when liquid glucose is being produced. For the preparation of solid glucose, the operation is continued until no further matter is precipitated in the alcohol test; a further 10 minutes' heating is then given to complete the conversion of the matter which is not precipitated by the alcohol. The most economic time-pressure values for maximum dextrose production from maize have been worked out by R. C. Ernst, C. E. Brown and J. B. Tepe.³⁴

The mass is neutralised with soda ash, insoluble matter is removed by filtration, and the liquor is concentrated to a density of about 30° Bé. The resulting syrup is passed through a battery of three decolorising tanks connected in series, and filled with animal charcoal. The colourless liquid is further evaporated under vacuum to a syrup of $42-45^{\circ}$ Bé. If it has been arranged for the necessary amount of dextrin to be left in, no crystallisation takes place, otherwise on cooling white or pale-coloured masses of sugar separate; or if anhydrous dextrose is desired, the warm syrup is thoroughly seeded with a small quantity of anhydrous glucose, and the mass allowed to crystallise. The crystals are separated from the mother-liquor by centrifuging. To prepare the monohydrate the liquor is 'seeded' with monohydrate crystals.

M. S. Badollet and H. S. Paine¹⁴ point out that neutralisation of the acid with sodium carbonate brings about clarification, as

the isoelectric point of the bulk of the colloidal matter present is reached at neutrality. Some colloidal matter, however, still remains dispersed, and the above workers, finding that this has a positive charge, have added such materials as bentonite, colloidal aluminates, aluminium silicate, and other colloidal clays and earths, which have a negative charge at the pH value of the acid starch-conversion liquors. They find that the bentonite flocculates the colloidal matter present in the converter liquor, and that settling out is more rapid and efficient than when sodium carbonate is



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FIG. 4:3.—Two rows of dextrose crystallisers.

used. Bentonite also eliminates the defect experienced with sodium carbonate, viz. that an excessive amount tends to re-disperse the colloidal material. This treatment prepares the liquor better for the bone-char filtration, and tends to reduce the rate of exhaustion of the bone-char. Sodium aluminate used in this way appears to be commercial practice, the results being reported satisfactory in the production of corn syrup and corn sugar.

Fellars, Millar, and Onsdorff¹⁵ found that dextrose syrups heated to high temperatures tended to darken, the colour effect being largely dependent on the pH value of the solution. W. Kröner and H. Kothe¹⁶⁻¹⁷ find that at temperatures over $100^{\circ}C$. this darkening is a function of the temperature, and deviations from proportionality between the glucose concentration and dis-

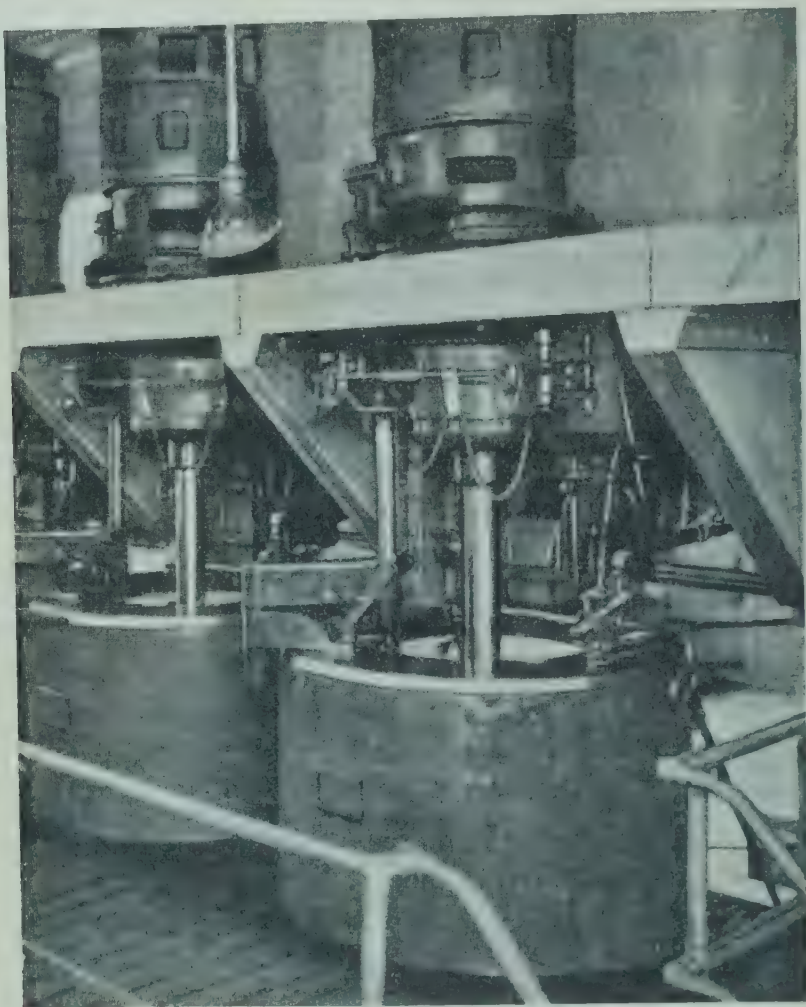
coloration are due to the effect of the sugar on the pH value of the solution. A sharp minimum occurs at pH 2.3-3.0. Unbuffered alkaline sugar solutions attain, after heating, a constant pH of 3.3 (in air) or 3.8 (air excluded). Under the conditions they employed, heavy metal salts had little effect on the discoloration, which was, however, increased in the presence of amino-acids, possibly owing to their effect on the pH of the solution. The discoloration due to the presence of proteins appears to be purely additive.

In further work²⁸ the starch was hydrolysed with hydrochloric acid at a given pH value at temperatures between 102-170° C. and a definite degree of discoloration of the solutions was produced for a given production of reducing sugar, irrespective of the temperature; the colour production was low in the early stages of the hydrolysis but increased rapidly later. Again, at pH 0.6-1.75 a similar relation exists between the amount of discoloration, measured as the extinction coefficient and sugar production so long as complete hydrolysis is not reached. Increase of colour is very rapid after the hydrolysis has been completed. Proportionality between the starch concentration and the colour developed could not be established, but it was noted that inferior starches gave more colour than good grade starches under similar conditions. The colour of the sugar solution is deepened on neutralisation and this appears to be due to the colouring matter acting as an indicator with a transition point between pH values of 4.5 and 6.5.²⁹ The technical implications of the above results are fully discussed by these workers with especial reference to the choice of acid concentration, temperature and time of heating and the starch concentration, and for these the reader is referred to the original papers.

One process of purification, introduced by Duryea,¹⁰ is to treat the liquor from the converters with 1 part tannin to every 4.800 parts liquor, heat to 90° C., filter, treat with animal charcoal, and concentrate. The corn syrup contains about 40 per cent. of dextrin, and, according to H. Berlin,¹³ the final mother-liquor from solid glucose manufacture contains about 70 per cent. glucose, 18.3 per cent. gentiobiose, which has probably been formed by reversion, and 12 per cent. of some other non-fermentable matter. In order to repress, to a great extent, the formation of gentiobiose and other condensation products, which appear to be formed during the later stages of the saccharification, and to remove traces of heavy metal salts, E. C. R. Marks²⁷ interrupts the conversion when about 40-42 per cent. of sugar has been formed, adjusts the pH value to between 4.5 and 4.8, filters, readjusts to pH 5.5-6.5, concentrates to d -1.2-1.26 and again

filters through bone-char. After dilution and re-acidification the conversion is completed.

The Crystalline Forms of Anhydrous Dextrose and

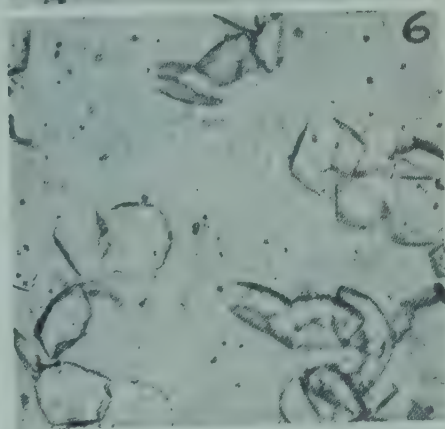
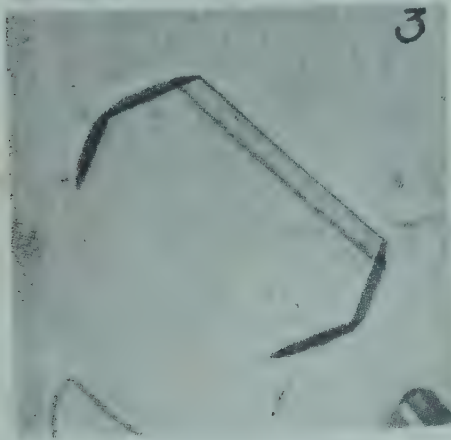
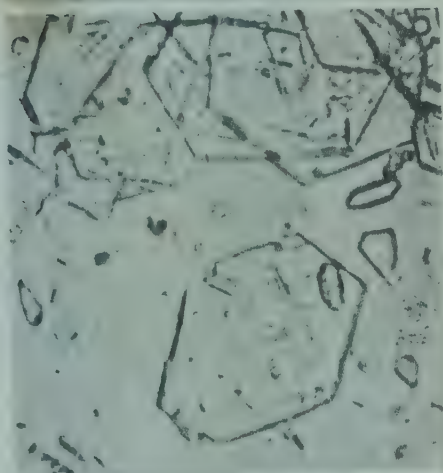
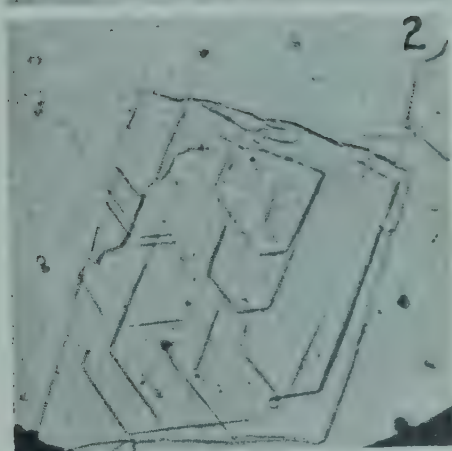
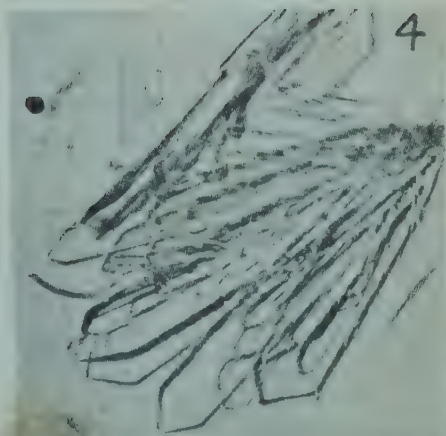
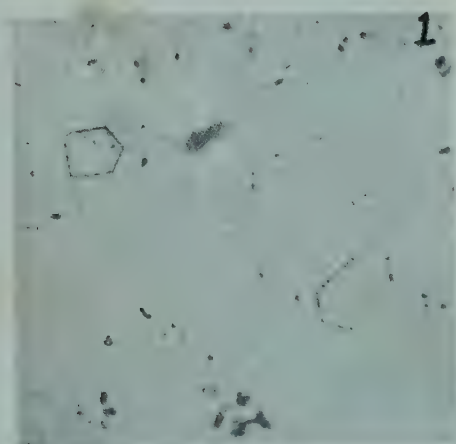


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FIG. 4:4.—Electric high-speed centrifugals. Bronze and monel metal construction.

Dextrose Hydrate.—W. B. Newkirk^{35, 36} set out to improve the method of Porst and Mumford³⁸ for producing chemically pure dextrose in which the crystallisation is carried out in the quiescent state to form a semi-solid mass which is paddled and then centrifuged. The difficulties with this method is the long time of centrifuging, the retention of mother-liquor, washing difficulties leading to the retention of 10-20 per cent. water.

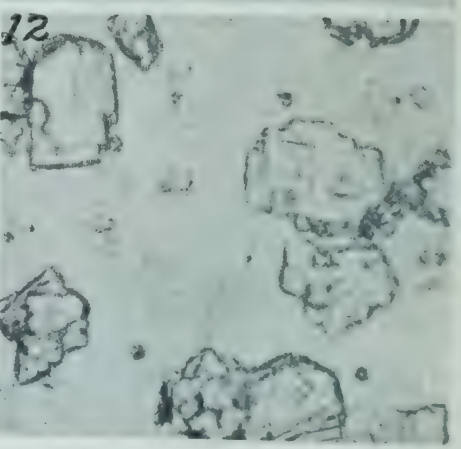
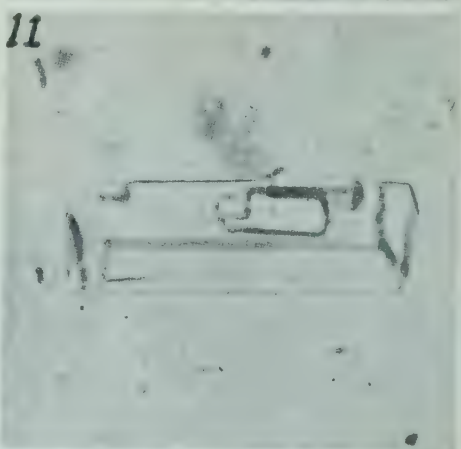
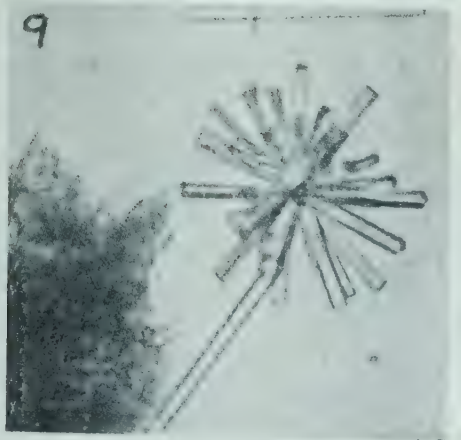
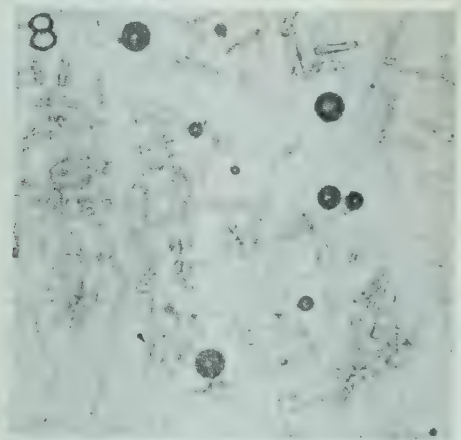
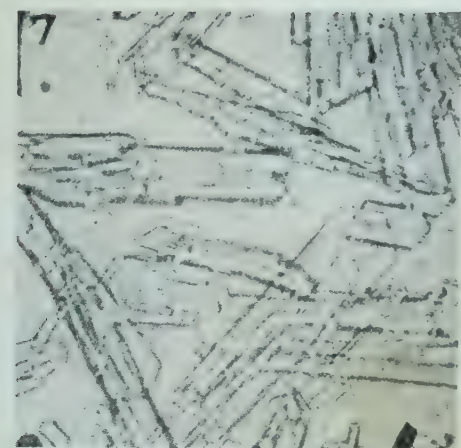
Becke was the first to record³⁹ the extremely thin, fragile,



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FIG. 4:5.

[Facing p. 70.



[Reproduced by courtesy of 'Industrial and Engineering Chemistry'.
FIG. 4:6.

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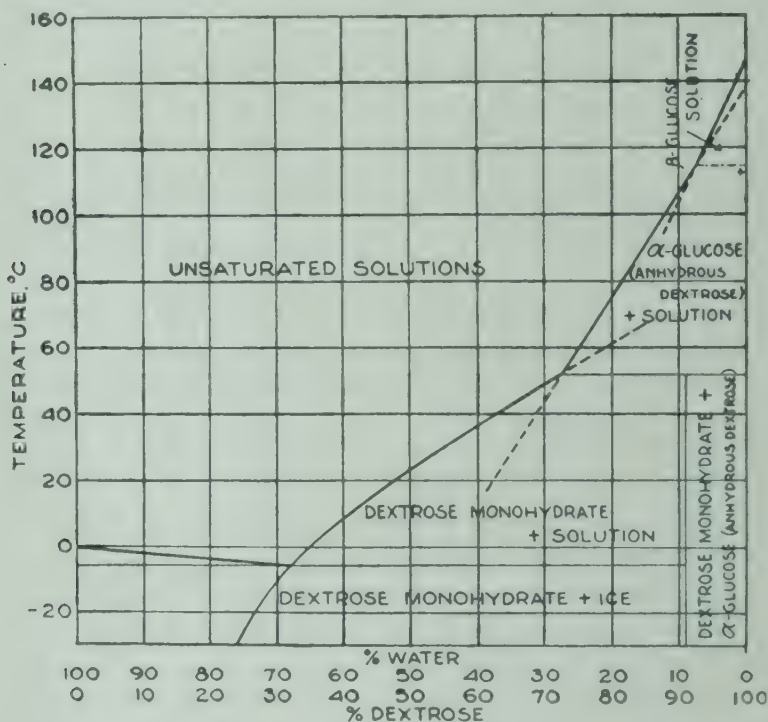
leaf-like pentagonal crystal of dextrose hydrate shown in the Photomicrographs Nos. 1 and 2, Fig. 4:5, taken by Sjoström and published by W. B. Newkirk,³⁵ the first being from hydrol, the final liquor of the process, the second from honey. In order to get good quick washing the type of crystal shown in Photomicrograph No. 3 is ideal and is produced by the twinning of two of the hemimorph forms after a rotation of 180° . The shape of the crystal is affected to a great extent by the conditions of crystallisation. *Still crystallisation* of normal factory liquors produces 'wart-like aggregations'³⁹ or aggregates resembling a sea-urchin³⁵ shown in Photomicrograph No. 4. These masses readily break down on centrifuging, forming a compact mass difficult to wash without waste. Photomicrograph No. 5 shows a typical hexagon crystal which gives a readily centrifuged and washable product, and Photomicrograph No. 6 shows the striking effect of the presence of impurities on crystal growth. The crystals here are almost perfect hexagons, thicker than those in Photomicrograph No. 5, and the top and bottom faces are lenticular instead of flat, thus preventing aggregation.

By *crystallisation in motion* long, thin, mechanically weak crystals are obtained (Photomicrograph No. 7, Fig. 4:6), and Behr⁴⁰ had suggested that *absolutely* quiescent conditions were required to obtain anhydrous crystallisation from convertor liquors. As Newkirk has pointed out, both the anhydrous and the hydrate forms can be produced simultaneously in the same liquor under these conditions. Photomicrograph No. 8 shows Behr's anhydrous dextrose, and No. 9 shows the dual crystallisation, whilst No. 10 shows anhydrous but weak dextrose crystals from strongly-agitated high gravity liquors. The true anhydrous crystal from water solution is shown in No. 11, and with proper gravities for slow motion Newkirk finds there are conditions between the anhydrous form shown in No. 8 and those in No. 11 which allow of easy washing, but another difficulty was then met.

In Fig. 4:7 the anhydrous α -dextrose solubility curve is quite steep, showing that either heavy gravities must be used, with the danger of forming crystals as in Photomicrograph No. 10, which is undesirable, or lighter gravities may be used and the final temperature lowered with the danger of producing dextrose hydrate. As anhydrous dextrose deposits the liquor becomes lighter in gravity and the forced cooling of the crystalliser reduces the temperature. If hydrate is made in the same building spontaneous seeding will find the right conditions present at this point to induce rapid hydrate formation, preventing adequate washing and causing solidification of the mass in the plant. The

best condition for obtaining easily washed, anhydrous, hydrate-free crystals (Photomicrograph No. 12) are obtained by the use of vacuum pans as crystallisers, where light-gravity liquors of low viscosity can be crystallised by some withdrawal of water without finishing in low temperature conditions.

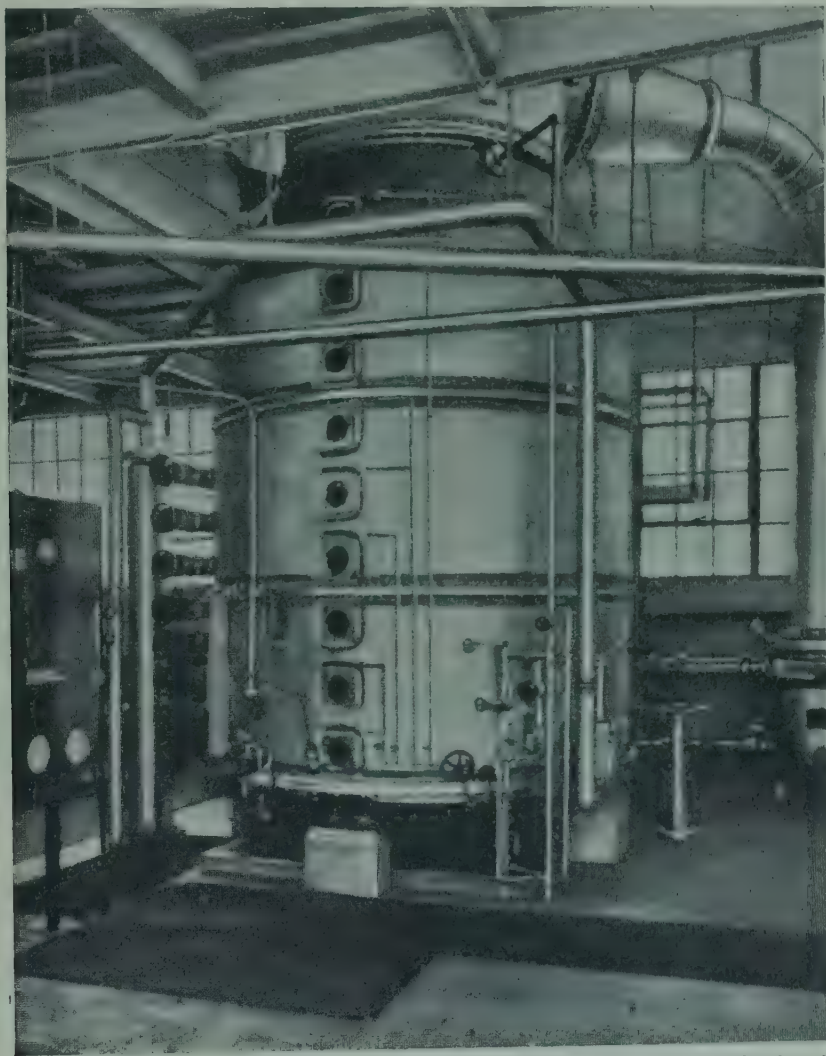
Producing Anhydrous Dextrose.—Besides the two α -dextrose crystals which give trouble, anhydrous β -dextrose is present and can be crystallised out, for the solution contains an equilibrium



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FIG. 4:7.—Phase diagram of dextrose solubility.

between the α - and β -isomerides. In this process it is necessary to have supersaturation of 5-8 per cent. to obtain crystallisation, and it must be supersaturation of the required isomer. The speed of mutarotation is also very important as anhydrous α -dextrose cannot be deposited quicker than it is formed. Strict control of the gravity, temperature and amount and distribution of the solid nuclei induced at the graining state is important. W. B. Newkirk^{35, 36} has described the process used at the Corn Products Refining Co. at Argo, U.S.A. Centrifugally washed hydrate (Cerelease) instead of being dried is dissolved to give a solution of 28-30° Bé. and treated for 30 minutes at 160° F. with 0.8 per cent. of Darco (carbon) on the weight of solids. The

liquor is then filter-pressed, any cloudy liquor being recirculated through the press until delivered clear. The liquor, after further filtering through streamline filters, is delivered to a copper or brass strike pan, sufficient liquor being led in so that by the



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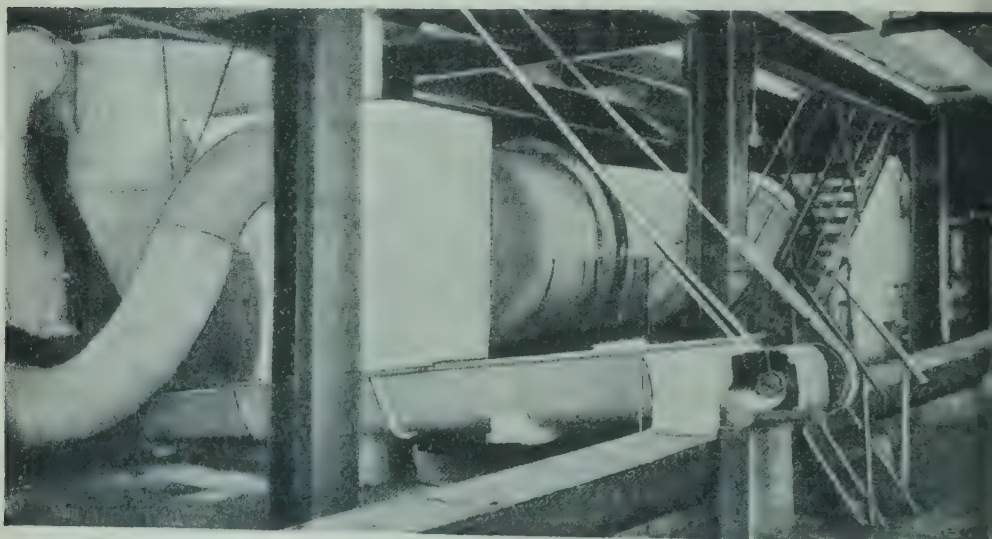
FIG. 4:8.—Brassery stallising pan used in anhydrous dextrose manufacture.

time the charge has reached graining conditions some 15-20 per cent. of the volume of the finished strike is present. The grain is taken in by gravity alone and without seeding, and after introduction of the grain a relatively large charge of 30° Bé. liquor is run in until the pan is approximately full and the strike is boiled on water. The finished strike is then fed into the brass centri-

fuges and the cake washed with hot water to prevent the mother-liquor becoming cooled and therefore supersaturated with respect to hydrate dextrose. The crystals then go to the dryer-granulator from which they are discharged as pure anhydrous dextrose.

W. B. Newkirk¹² hydrolyses the starch as far as possible, filters the liquor through bone-char, and after concentrating, allows it to crystallise at 38°C . with stirring. The mother-liquor is separated by centrifuging, and the crystals, after washing with water, should have a purity of 99-100 per cent.

The Chemistry of Glucose Manufacture.—Since starch is not a single entity but a mixture of two compounds the issues



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FIG. 4:9.—Dextrose dryer.

affecting its conversion to glucose by acid hydrolysis have been clouded. In addition starches from various sources may contain esterified phosphoric acid, fatty acids and proteinous compounds. Theoretically the conversion of starch to glucose is the summation of the hydrolysis of amylose and of amylopectin but no information is available on the fundamental studies of the acid hydrolysis of amylose and of amylopectin since their separation in the practically pure form is a matter of comparatively recent history. Some of the glucosidic linkages in starch do, however, appear to be more readily hydrolysed than others and may account for the more rapid hydrolysis apparent in the first stages of the process. The comparative ease of cleavage of the 1·4 and the 1·6 glucosidic linkages is still a matter of controversy,⁴¹⁻⁴³ but this will have an influence on the course of the reaction.

Although glucose is the main product there may be varying quantities of gentiobiose, levulinic acid and furfural derivatives and other degradation products or condensation products.

H. Berlin¹³ has indicated that the gentiobiose is formed by the rejoining of two glucose units by a 1·6 β -glucosidic bond and it is by no means unlikely that a glucose unit may not condense with a maltose molecule by a 1·6 β -glucosidic bond in a similar manner. The mother-liquor from glucose manufacture, or 'hydrol,' can be re-treated to produce a further yield of dextrose, such treatment hydrolysing the 1·6 bond in the gentiobiose present to give two molecules of dextrose again.⁴⁴⁻⁴⁵

Moyer⁴⁶ has discussed the production of levulinic acid by the action of acid on starch and dextrose and Kerr⁴⁷ considers that this may be formed via methyl hydroxy furfural. These substances may form polymers of unknown composition.

Since these secondly mentioned compounds are formed in but small amounts (less than 1 per cent.) the efficiency of the conversion of starch to dextrose is chiefly improved in practice by choosing such conditions that the equilibrium point of the dextrose \rightleftharpoons gentiobiose reaction is moved in favour of the dextrose, e.g. by keeping the concentration of dextrose down to the practical minimum.

Freudenberg and Kuhn, assuming the hydrolysis to be a monomolecular reaction involving the scission of equivalent 1-4 α -glucosidic bonds, apply a simple statistical treatment to predict values to be obtained for glucose, maltose and higher homologues at any given time in the early stages of hydrolysis. Analytical values, however, do not confirm that the reaction is one of random hydrolysis of equivalent glucosidic linkages and it would appear that such a suggestion is an over-simplification of the actual course of the reaction. The analyses are difficult to make and the methods^{48,52} are discussed fully by Cantor and Moyer⁵³ who checked Freudenberg's and Kuhn's equations. They found maltose had a higher hydrolysis rate than starch which led them to suggest that the terminal glucose unit is more readily hydrolysed.

Sadovy⁵⁴ has followed the hydrolysis of starch by acid using the iodometric method to determine liberated aldehyde groups.⁴¹ He found the rate of hydrolysis proportional to the acid present but as his range of concentrations of hydrochloric acid was limited the relationship can hardly be expected to hold at extreme acid concentrations where the activity of the acid would be a deciding factor.

That starch can bind acid^{55,56} and that buffering agents may be present in the raw starch, has an influence on the activity of

the added acid so that the effect of the latter differs from what might have been expected. Adsorption of cations by starch has been discussed in Vol. I and by Samec⁵⁷. The natural cations of starch become replaced during processing in starch manufacture with sodium ions, especially when zeolite-softened water is used and such starch gives hydrolysis liquors with a smaller tendency towards turbidity since less insoluble sulphate is present.

In potato starch the phosphoric acid liberated assists in buffering the solution and in the case of maize the presence of protein matter exerts a like effect, although a little phosphoric acid may also be present derived from the hydrolysis of phytin in the maize kernel. All these factors vary, not only from starch to starch but from one sample of starch to another of the same starch. Thus to obtain the best control of the process in glucose manufacture it is preferable to make periodic determinations of the acid binding power of the starch used. Since sodium chloride and other electrolytes have a marked effect on the activity of the acid used their amount is important when it is desired to compute the rate of hydrolysis after a given addition of acid.

Moelwyn-Hughes⁵⁹ has examined the dextrose \rightleftharpoons gentiobiose equilibrium and from his work it appears that the higher the temperature the more the equilibrium moves to the left so that high converting temperatures are detrimental to high yields. Silin and Sapedina⁴⁴ in their studies of the reaction find that the use of high starch concentrations lead to reduced yields of glucose. Thus the use of a 25 per cent. starch concentration would give 13.2 per cent. lower yield of glucose than if the initial starch concentration was 15 per cent. In U.S.A. even lower initial starch concentrations are common practice.

Uses of Glucose.—Most of the sales of refined dextrose made from corn sugar in the U.S.A. is absorbed by the food industry. The free use of dextrose in the U.S.A., without declaration on the label, was authorised by the Secretary of Agriculture in 1930.

Many canned goods are improved by using pure glucose² instead of sucrose. The optimum amounts used vary from 20-50 per cent. of the total sugar present; it cannot be used in concentrations over 50 per cent. because it crystallises out. Canned prunes, plums, rhubarb and apple sauces, tomato juice, sweet pickles, sweet and sour cherries (excluding black, sweet varieties), apricots, and some varieties of peaches are improved by 20-40 per cent. of 'Cerelese'. With peas, beets, apple butter, strawberry and pineapple preserves, citrus marmalade, cranberry sauce, currant, apple and quince jellies, some of the sucrose may

be replaced by pure glucose without impairing the flavour or quality.

The addition of 1 per cent. pure glucose to cucumber pickle brines accelerates fermentation, produces a higher final acidity, and aids in maintaining an active flora of lactic bacilli.

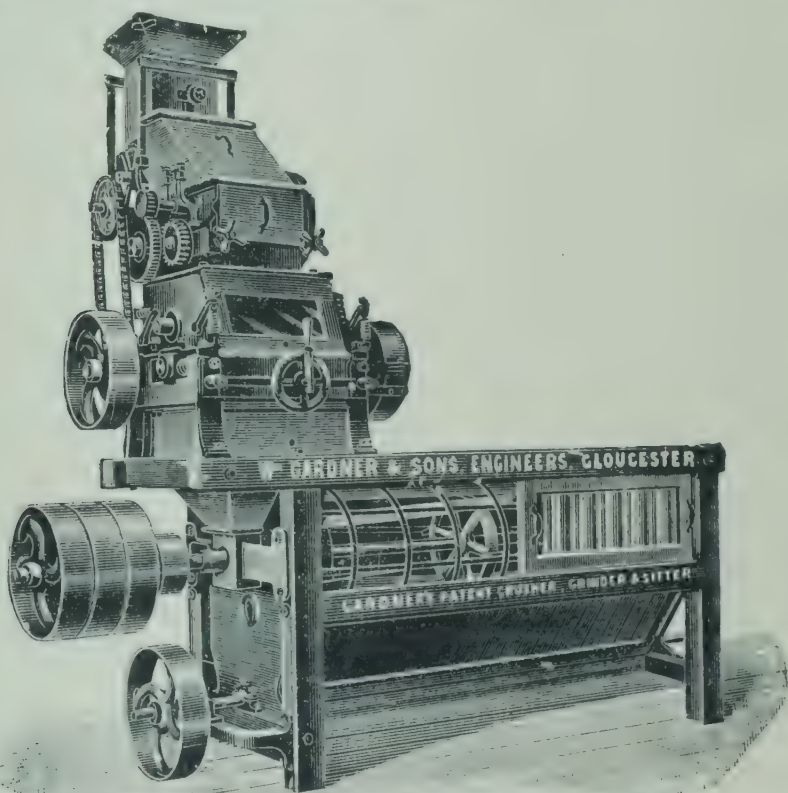
Glucose is also widely used in the manufacture of confectionery, mixtures of glucose and sucrose being 'boiled' together until the correct properties have been imparted to the mass, which is then coloured with pure dyestuffs and formed into 'sweets'. According to the type of boiling, and the process to which the boiled sugar is subjected, boiled 'sweets' and those of the fondant type are produced. Recently, beet sugar has been widely employed instead of corn glucose, with excellent results when care has been taken to make slight adjustments in the process to allow for the greater content of sulphur dioxide in the beet sugar.

Further uses of glucose are as a conditioning agent in dressings and sizes, and in adhesives.

Glucose is also used as the starting-point for the manufacture of certain industrial chemicals. Gluconic acid is obtained by fermenting glucose solutions with the culture of *Penicillium leteum purpurogenium*. The conditions of the action, e.g. pH value of the medium, are carefully regulated, and a 60 per cent. yield of gluconic acid is obtained in a manufacturing cycle of 11 days. P. A. Wells and G. E. Ward³¹ have given an excellent résumé of the uses of glucose in the fermentation field in which they deal with bacterial fermentation to yield lactic acid (see also p. 97) and the production of gluconic acid by submerged and surface fermentations. It is of interest that by submerged fermentation, using rotary fermenters, with an air pressure of two atmospheres they found *Aspergillus niger* gave a practically quantitative conversion of 20 per cent. glucose solutions to gluconic acid in 24 hours instead of the more usual 60 per cent. yield obtained in 10 to 12 days by the usual methods. The electrolytic method of producing gluconic acid has now been displaced in America by the fermentation process, and in 1939 some 500,000 lb. of calcium gluconate was produced in the U.S.A. (see also p. 102). A. J. Moyer and co-workers^{32,33} have dealt at some length with the production of gluconic acid by the method of submerged growth under increased air pressure; and according to some work by the U.S. Dept. of Agriculture the addition of a small amount of boric acid or borax promotes the biochemical reactions partly by keeping the calcium gluconate in solution. Kojic acid is produced in 50-60 per cent. yields by the action of *Aspergillus flavus* on glucose solutions.³¹ Recently,^{18,25}

sorbitol and mannitol have been manufactured from glucose by an electrolytic method, and the former is already finding an outlet as a humidifying agent, softener and plasticiser. Citric acid has also been manufactured from glucose.¹⁹

The Manufacture of Maltose.—By treating starch paste with malt diastase, maltose may be obtained in a yield of about 80 per cent., 20 per cent. of dextrans being produced simultaneously. This enzyme action was first recorded by Irvine in



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FIG. 4:10.—Sugar grinding and sifting machine.

1785, but it was not until 1819 that de Saussure²⁰ isolated maltose from the products of this reaction and obtained the sugar in a crystalline form. Later, it was re-examined by Dubrunfaut,²¹ who named it 'maltose'. These observations passed unnoticed until 1872, when C. O'Sullivan²² rediscovered it and carried out further work.

Dubrunfaut, after his initial examination of the reaction, worked with Cuisinier and together they patented a process for preparing maltose in a crystalline state or as a syrup, these products being intended for use in distilleries and breweries for sweetening

wines, making liqueurs, or for brewing. In their method a starch paste was prepared by heating starch and water together, and this was treated at 70-80° C. with 5-10 per cent. of a 'green' malt infusion in order to liquefy it; the mass was slightly acidified with hydrochloric acid and converted to a maltose-dextrin mixture at 50° C. with from 5-20 per cent. of a diastase preparation. The solution was filtered and allowed to stand for 15 hours, concentrated, refiltered and then further concentrated. After a treatment with animal charcoal, the liquid was crystallised.

As these workers used crude raw materials, such as ground maize, the pastes obtained in their process were too thick to handle easily and, owing to the difficulty of obtaining a homogeneous distribution of the diastase preparation and of the 'green' malt, excessive amounts of these had to be employed to carry the reaction to the required stage in an economic time. The presence of extraneous substances in the flours used also contributed largely to difficulties in refining the syrups obtained. In order to get thin fluid pastes in the first instance, weaker starch pastes had to be employed, which led to excess costs for evaporation. These factors, in addition to the competition from glucose, which by then was being produced by the well-established and economic saccharification of starch by acids, contributed to the commercial failure of the process.

A better process is that introduced by Duryea²⁶ in which a thin-boiling starch solution of 16° Bé. is treated with malt extract at 59° C.

Ptyalin, an enzyme present in saliva, also rapidly effects the conversion of starch into maltose; pancreatin has a similar action, but the reaction is carried further to produce glucose.

To prepare pure maltose, barley diastase may be used instead of malt diastase, with the consequent avoidance of the formation of alcohol-soluble dextrans, which would cause trouble in the purification processes.²³ Pure maltose may be obtained²⁴ by digesting crushed barley with 2-4 parts of 20 per cent. alcohol for 24 hours, filtering off the liquid and precipitating the diastase by the addition of twice its volume of absolute alcohol. The precipitate is washed with absolute alcohol, then with ether, and finally dried *in vacuo* over sulphuric acid. Fifty grams of starch are heated with 1,600 ml. of water, and the paste treated with 1 gram of the diastatic preparation for 5-6 hours at 50° C., the temperature being allowed to fall to room-temperature at the end of this time, and the action allowed to continue for a few more hours. After evaporating the product to a syrup, it is poured into industrial spirit until the strength of the latter has fallen to

about 80 per cent. The precipitated dextrans, etc., are filtered off and the liquid evaporated to a thick syrup, which is seeded with a crystal or two of pure maltose and then set aside to crystallise. The crystals so obtained may be further purified by washing with absolute alcohol, redissolving in a little water, re-treating with industrial spirit, filtering, and evaporating. The resulting maltose readily crystallises from strong aqueous solutions. Maltose has no extensive industrial uses.

REFERENCES

1. T. DE SAUSSURE, *Bull. Pharm.*, 1814, **6**, 499.
2. C. R. FELLARS, *Div. Agric. Food Chem. Symposium, Amer. Chem. Soc.*, 1937.
3. W. EKHard, *Zeit. Spiritusind.*, 1923, **46**, 228.
4. E. PREUSS, *ibid.*, 1904, **27**, 478.
5. E. PAROW, *ibid.*, 1922, **45**, 229.
6. C. B. DURYEA, E.P. 11,800 and 11,801, 1907.
7. A. SEYBERLICH and A. TRAMPEDACH, E.P. 8,000, 1885.
8. F. MALINSKY, *Zeit. Spiritusind.*, 1899, **22**, 240.
9. H. J. HADDON, E.P. 6,176, 1882.
10. C. B. DURYEA, E.P. 280,680, 1927.
11. E. PAROW, *Zeit. Spiritusind.*, 1905, **28**, 121.
12. W. B. NEWKIRK, U.S.P. 1,471,347, 1923.
13. H. BERLIN, *J. Amer. Chem. Soc.*, 1926, **48**, 2627.
14. M. S. BADOLLET and H. S. PAINE, *Ind. Eng. Chem.*, 1927, **19**, 1245.
15. C. R. FELLARS, J. MILLAR, and T. ONSDORFF, *ibid.*, 1937, **29**, 946.
16. W. KRÖNER and H. KOTHE, *Zeit. Spiritusind.*, 1937, **60**, 191, 199 and 207; *ibid.*, 1938, **61**, 209, 217 and 227.
17. — *Ind. Eng. Chem.*, 1939, **31**, 248.
18. R. L. TAYLOR, *Chem. Met. Eng.*, 1937, **44**, 588.
19. CHAUNCEY CHEM. CO., F.P. 819,279.
20. T. DE SAUSSURE, *Phil. Trans. Roy. Soc. Lond.*, 1819, **109**, 29.
21. A. P. DUBRUNFAUT, *Ann. chim. d. phys.*, 1847, **21**, 178.
22. C. O'SULLIVAN, *J. Chem. Soc.*, 1872, **25**, 579.
23. J. L. BAKER and F. DAY, *Brit. Assoc. Rep.*, 1908, 671.
24. C. J. LINTNER, *J. prakt. Chem.*, 1886, **34**, 386.
25. L. LIGHT, *Chem. Age*, 1936, **34**, 531.
26. C. B. DURYEA, *J. Ind. Eng. Chem.*, 1914, 419.
27. E. C. R. MARKS, E.P. 291,991, 19/8/1927.
28. H. KOTHE and W. KRÖNER, *Zeit. Spiritusind.*, 1939, **62**, 191, 197, 205, 213.
29. — *ibid.*, 1939, **62**, 245, 253.
30. L. E. STOUT and C. G. RYBERG, *Ind. Eng. Chem.*, 1939, **31**, 1451.
31. P. A. WELLS and G. E. WARD, *ibid.*, 1939, **31**, 172.
32. A. J. MOYER *et al.*, *Ind. Eng. Chem.*, 1937, **29**, 777.
33. — *ibid.*, 1937, **29**, 653.
34. R. C. ERNST, C. E. BROWN and J. B. TEPE, *ibid.*, 1939, **31**, 1247.
35. W. B. NEWKIRK, *Ind. Eng. Chem.*, 1936, **28**, 760.
36. — *ibid.*, 1939, **31**, 18.
37. — *ibid.*, 1924, **16**, 1173.
38. C. E. G. PORST and N. V. S. MUMFORD, *ibid.*, 1922, **14**, 217.
39. F. SOXHLET, *J. prakt. Chem.*, 1880, **21**, 242.
40. A. BEHR, *Ber.*, 1882, **15**, 1104.
41. M. LEVINE, J. F. FOSTER and R. M. HIXON, *J. Amer. Chem. Soc.*, 1942, **64**, 31.
42. R. W. KERR and N. F. SCHINK, *Ind. Eng. Chem.*, 1941, **33**, 1418.
43. K. MYRBÄCK, *Svensk. Kem. Tid.*, 1941, **53**, 264.

44. P. M. SILIN and E. A. SAPEDINA, *Rev. Voronezhshsky Chem. Tech. Food. Ind.*, 1939, **3-4**, 79.
45. C. EBERT, W. B. NEWKIRK and M. MOSKOWITZ, U.S.P. 1,704,037, 1929.
46. W. W. MOYER, Paper presented at Amer. Chem. Soc. meeting, Memphis, 1942.
47. R. W. KERR, *Chemistry and Industry of Starch*, Academic Press Inc., N.Y., 1944.
48. K. SICHERT and B. BLEYER, *Z. anal. Chem.*, 1936, **107**, 328.
49. C. D. HURD and S. CANTOR, *J. Amer. Chem. Soc.*, 1938, **60**, 2677.
50. — R. W. LIGGET and K. M. GORDON, *ibid.*, 1941, **63**, 2656.
51. — and K. M. GORDON, *ibid.*, 1941, **63**, 2657.
52. — and R. W. LIGGET, *ibid.*, 1941, **63**, 2659.
53. S. CANTOR and W. W. MOYER, Paper presented at Amer. Chem. Soc. meeting, Buffalo, 1942.
54. J. E. SADOVY, *Res. Voronezhshsky Chem. Tech. Inst. Food. Inst.*, 1939, **3-4**, 89.
55. P. M. SILIN, *Reviews of the Tomskey Technical Inst.*, 1924.
56. WIDMEYER and RALL, *Memoirs, Peoples Inst. Starch and Food Res.*, 1931.
57. M. SAMEC, *Kolloidchemie der Stärke*, Dresden, 1927.
58. A. THOMPSON, U.S.P. 2,206,311, 1940.
59. E. A. MOELWYN-HUGHES, *Trans. Farad. Soc.*, 1929, **25**, 86.

ADDITIONAL REFERENCES

- H. F. BAUER, *Eighth Inter. Congr. Appl. Chem.*, 1912, **13**, 21. (Preparation of chemically pure glucose from commercial product.)
- E. PAROW, *Zeit. Spiritusind.*, 1921, **44**, 177, 187. (Discusses American technique for making glucose.)
- J. K. DALE, *Chem. Age*, 1923, **31**, 295. (Manufacture of glucose.)
- A. E. WILLIAMS, *Ind. Chemist*, 1930, **6**, 495. (Manufacture of glucose.)
- W. B. NEWKIRK, E.P. 246,098, 11/8/1925. (Production of crystalline dextrose.)
- C. B. DAVIS, U.S.P. 1,618,148, 1927. (Colloidal tannate of iron added to precipitate electropositive colloids.)
- W. R. FETZER, U.S.P. 2,210,659, 6/8/1940. (Some glucose returned to next batch to reduce reversion products formed.)
- CORN PRODUCTS Co., LTD., E.P. 536,020, 1941. (Glucose produced from potatoes without first separating starch.)
- J. L. BAKER, B.P. 564,895, 18/10/1944. (Process of manufacture of maltose from starch described.)
- N. HOŠPES, *Z. Spiritusind.*, 1941, **64**, 147. (Discusses discoloration of glucose due to heat and storage.)
- TSENG-JO SUEN and TSEN-PU Chien, *J. Chem., Eng., China*, 1941, **8**, 19; via *Amer. Chem. Abst.*, 1943, **37**, 1076. (The kinetics of hydrolysis of various starches with dilute sulphuric acid at various temperatures and concentrations discussed. Reaction is of first order and reaction velocity constant varies with the starch used. Reaction velocity doubles with 5° rise in temperature.)
- W. KRÖNER, W. REISCHEL and W. HÖPPNER, *Z. anal. Chem.*, 1941, **122**, 321. (Determinations of dry substance in starch-sugar juices and starch syrups discussed. Abbé-refractometer most suitable in conjunction with density determns. using pycnometer.)
- W. B. NEWKIRK, B.P. 232,160, 22/9/24. (Method of 'seeding' dextrose liquors to obtain crystals described.)
- J. F. WALSH, U.S.P. 2,223,925. (Preparation of non-caking, spray-dried, starch conversion product claimed.)
- LAMPITT *et al.*, *J. Soc. Chem. Ind.*, 1947, **66**, 68. (Determination of dextrose and maltose with ferricyanide-carbonate reagent.)
- W. R. FETZER, U.S.P. 2,393,095, 15/1/1946. (Claims process for dextrose from starch which is cyclic in operation and avoids accumulation of ash in the liquors.)

- N.V.O.J. Mayer's Dextrinfabrik., Dutch Pat., 56,315, 15/5/1944. (Starch suspension introduced into hydrolysing liquor under surface and near steam supply to produce dextrose.)
- A. E. WILLIAMS, *Synthetics and By-products*, 1946, 8, 235. (Discusses manufacture of crystalline dextrose.)
- A. S. SIPYAGIN, U.S.S.R. Pat., 65,092, 31/8/1945. (Fresh starch added to partially converted liquor and saccharification completed.)
- A. E. A. BEAVER, B.P. 561,706, 1/6/1944. (Starch treated with enzyme from *B. subtilis* and then with malt extract.)
- K. A. CLENDENNING and D. E. WRIGHT, *Can. J. Research*, 1948, 26F, 284. (Pilot plant production of syrups from wheat, potato, tapioca and waxy cereal starches described.)
- K. A. CLENDENNING, *ibid.*, 1948, 26F, 277. (Control of copper corrosion in starch-syrup manufacture discussed. Copper in syrup determined by pptn. with salicylaldoxime without ashing.)
- J. F. WALSH, U.S.P. 2,245,309, 10/6/41. (appl., 26/4/40.) (Conversion syrup vacuum-evaporated to 1-4 per cent. moisture content then chilled and solidified by pouring into water at 0.5° C. Solid quickly separated and dried in hot air at 75° C. and 15 per cent. R.H.)

CHAPTER 5

THE PRODUCTION OF CHEMICALS FROM STARCH BY FERMENTATION PROCESSES

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Introduction.—Of the natural phenomena that constitute the basis for man's existence, none is more impressive in magnitude and in character than is the annual production of several billions of tons of sugars, starches and cellulose by photosynthetic processes. From these materials man obtains much of his food, shelter, raiment and fuel. These are also the raw materials for the fermentation industries, by which man obtains chemicals of growing importance to his well-being. At present he uses only about two million tons per year for such operations, less than 0.1 per cent. of the total supply, but the chemicals produced have a large significance.

During the 25-year period prior to 1941, blackstrap molasses, a byproduct in cane sugar manufacture, was the principal source of carbohydrates for the fermentation industries and nearly the entire world production was used for such purposes, most of it in the United States. But the war demand for fermentation chemicals became so large, and ocean transport of molasses so difficult, that a sudden shift from blackstrap to grains became necessary and during the war period about three-fourths of the fermentation chemicals produced by the United Nations were made from grain starches.

Of course ethyl alcohol is the fermentation chemical made in largest volume, and its production has increased about sixfold since 1941 because of the large need for it in the war. But there are many other important fermentation chemicals, including n-butyl alcohol, acetone, glycerol, 2, 3-butylene glycol and acetic, propionic, butyric, lactic, citric and gluconic acids. Penicillin and other antibiotics are recent important additions to the fermentation chemical family. The index prepared by Fulmer and Werkman¹ presents a good picture of the wide diversity of products of the action of bacteria, yeasts and moulds upon carbohydrates and other substrates.

War Induced Expansion of the Fermentation Industry.—

The largest of the new markets for fermentation chemicals is in the manufacture of synthetic rubber. Nearly 60 per cent. of the annual production of synthetic rubber in the United States, which at the peak exceeded one million tons per year, was derived from butadiene made from fermentation ethyl alcohol, according to data presented in the report from the Rubber Reserve Company.² Fulmer³ has prepared an excellent review of the literature on synthetic rubber manufacture and has described the steps leading to the present industry.

Perkin and associates in England, in the first, commercial synthetic rubber programme, made butadiene from n-butyl alcohol produced from starch by fermentation. This enterprise was killed by a price war shortly before World War I. In Russia a strongly nationalistic programme protected the synthetic rubber activities and in 1931 the first pilot plant production was realised, using the Lebedeff process for the production of butadiene from ethyl alcohol. This operation was so successful that construction of commercial plants started six months later and 5,600 long tons were made in this way in 1933. Production reached 90,000 long tons in 1938, about three-fourths of Russia's total rubber requirement. Russia led the way in synthetic rubber manufacture, and fermentation ethyl alcohol was practically the sole source of the butadiene used to make this rubber.

Other countries followed the Russian activities and with modifications the Lebedeff process was employed in Poland, Czechoslovakia and Italy. Germany subsequently developed a different process in which butadiene was derived from acetaldehyde, which was made from ethyl alcohol, acetylene or heavy oils, depending upon their relative availability. This process was later applied in Japan. In the United States one industrial organisation developed improvements in the Lebedeff process, another successfully established the production of butadiene from petroleum hydrocarbons, and the rubber companies themselves developed improvements in the polymerisation of butadiene, especially with styrene or with acrylonitrile. Research on the development of compounding formulas was especially active in the United States after 1941, and some marked improvements were made. This research is making rapid progress at the present time.

The synthetic rubber programme of the United States was on a pilot plant basis only at the time enemy action shut off the primary supply of natural rubber and the first efforts of governmental agencies were directed toward developing a programme based

upon the manufacture of butadiene from petroleum hydrocarbons. The Gillette Committee of the United States Senate⁴ showed the inadequacies of that programme and recommended the immediate inclusion of provisions for additional grain alcohol manufacture and for its conversion to butadiene. Subsequently the Baruch Committee confirmed these findings and repeated the recommendations. As a result, early in 1943, a programme was initiated looking toward the production of butadiene from fermentation ethyl alcohol. A year later large-scale production was in progress and the factories have since reached production rates as high as 180 per cent. of the design capacity. This was very fortunate because the petroleum process had failed by quite a large margin to meet its schedule. This new market has been using about three times as much alcohol as was required for the total pre-war industrial markets in the United States. As previously noted, almost half the total butadiene production has been derived from fermentation alcohol, and the total synthetic rubber production has reached a level 50 per cent. above pre-war natural rubber importations.

One other use that became a major factor in the alcohol demand in 1944 was its employment as a supplemental fuel for aviation engines. A simple injector was developed that admits aqueous alcohol to the intake manifold when conditions are such as to cause detonation, the alcohol serving as an anti-knock agent and an internal coolant. This use has been described by Colwell, Cummings and Anderson.⁵ By late 1944 considerable quantities of alcohol were being used for this purpose. In Cuba, Brazil and elsewhere the use of alcohol in motor fuel blends has continued to expand, some blends containing as much as 65 per cent. of alcohol. The properties of alcohol-gasoline blends have been described by Howes,⁶ Taub,⁷ Brown and Christensen,⁸ Christensen,^{9,10} Jacobs and Newton,¹¹ Shepherd, McPherson, Brown and Hixon,¹² and Beresford and Christensen.¹³

The commercial production of penicillin and the development of intensive research on other antibiotics were spectacular features of the war programme. Prior to 1943 this industry was non-existent; by 1945 some 30 plants in England, Canada and the United States were producing at the rate of 100,000 million units per month.

Research on the manufacture of butadiene from 2, 3-butylene glycol was very active in 1942 and 1943, and much progress was made in the production of the glycol from various substrates, but the high degree of success of the alcohol-butadiene programme made it unnecessary to develop this process and by 1945 it was

generally conceded that the glycol could not find a place in the rubber programme for some time. Interest in 2, 3-butylene glycol for other purposes has continued and research is still active in several laboratories. The laevo form is a good non-evaporative antifreeze.

The demand for other fermentation chemicals has grown with the general chemical programme. Lactic acid production has expanded to supply the demands satisfied by importation in the pre-war trade, and research on acrylate plastics from alkyl lactates has yielded results of considerable interest. Increased post-war production seems probable.

Agriculture's Interest in the Fermentation Industry.—It is impossible to understand the significance of the fermentation industry as it is now operating, or to evaluate its post-war prospects, without giving careful consideration to its relation to agriculture, because the two industries are most intimately connected. This has been the subject of many technical and economic analyses and the reports by Hale,¹⁴ Christensen, Hixon and Fulmer,¹⁵ Shepherd, McPherson, Brown and Hixon,¹² Christensen,¹⁶ Willkie and Kolachov,¹⁷ and Filley, Loeffel and Christensen¹⁸ present the broad outlines of the foundation upon which a technically and economically sound industry can be built.

The cost of the fermentation chemical depends primarily upon the price that must be paid for the raw material, assuming good factory management. In producing the chemical from grains, all of the original raw material except the starch consumed is recoverable as a protein concentrate needed in feeding livestock. Then the cost of the starch is the difference between the price paid for the grain and the income from sale of the by-products derived from it, both of which are of vital interest to the farmer, who sells the grain and buys the residual solids.

What value should the farmer place upon this starch? That, of course, is determined by its value in other markets, by far the largest of which is livestock feeding. A rough generalisation that gives a good picture of the situation is afforded by the following simple analysis. Feed grains, such as corn, barley, rye and sorghums, contain approximately 1 part of protein for 10 parts of carbohydrate. A balanced feeding ration contains substantially 1 part of protein for 6 parts of carbohydrate. That is, these common feed grains contain too little protein or too much carbohydrate. The imbalance can obviously be corrected by adding protein or by subtracting starch. If grains are the only feed used, the protein-carbohydrate ratio can be corrected if the starch is removed from some part of the grain and the residue is combined

with the balance of the grain. Assuming that the original grain contains 10 per cent. of protein, the residual solids 30 per cent. and the desired blend 16 per cent., then the percentage of the grain that should be processed is

$$\frac{(16 - 10) \times 100}{30 - 10} = 30 \text{ per cent.}$$

But this result must be modified by the fact that other feed ingredients are used, some containing more protein than do the feed grains. Various estimates have been made showing that from 10 per cent. to 20 per cent. of the feed grains might be processed in the fermentation industry in the United States without using starch that has any real net value in feeding livestock; the farmer could actually give it to the factory without losing money, because it has no value in livestock feeding. This analysis indicates around 10 million tons of surplus starch in the feeding programme in the United States alone.

But there is no need for the farmer to give the starch to the factory, and undoubtedly he would not willingly do so. The sugar content of pre-war blackstrap cost the fermentation industry 1 cent per pound, and this surplus starch of grains therefore has substantially the same value in the competitive market. What this means in grain prices depends upon the composition of the grain and the value assigned to the residual solids. If, for example, a bushel of grain weighing 56 pounds yields 31 pounds of starch (or its equivalent as the products of fermentation) and 21 pounds of residual solids, then its value is 31 cents plus whatever value agriculture places upon the 21 pounds of residual solids. For a continued successful use of starch or starch-containing materials it is necessary that the fermentation industry and agriculture agree upon some such pricing plan.

World War 11 has shown quite clearly that many peoples have been living on a protein deficiency basis. Only a decade ago the agricultural areas were complaining of grain surpluses, but if the situation of that day is examined in the light of subsequent developments, it becomes quite evident that there never was a real surplus of grains, but rather the surplus of starch was allowed to reveal itself as an apparent surplus of feed grains. Properly co-ordinated, the fermentation industry, along with other starch-using industries, and agriculture can readily prevent any such situation developing again. The very large increase in agricultural production, about 25 per cent. in the United States since 1940,

creates a very favourable opportunity for the establishment of a sound co-operative programme of this character.

An Estimate of Post-war Trends.—The post-war economy has not yet stabilised in most of the world and no definite pattern has yet become apparent. Food and feed grains grown in the United States have been shipped to all parts of the world to feed starving peoples and their use in the fermentation industry has been greatly curtailed, often by governmental regulation.

Synthetic rubber continues to hold its place as the major raw material for most rubber goods in the United States, but it is being made primarily from petroleum. Alcohol supplies have been inadequate to permit widespread use of the injector as planned by the manufacturer. Molasses has again become available at low prices and is a major source of fermentation chemicals.

But as this is written, grain and other starchy farm crops are piling up large surpluses in the United States and in most other agricultural countries. They again seriously threaten the national economic stability and in these countries there is renewed interest in their conversion to fermentation chemicals.

The expansion in cellulose acetate, ethyl cellulose and other plastics using fermentation chemicals is likely to continue, but at a slower rate, into the post-war period. Acrylate plastics from lactic acid seem to be on fairly good grounds.

There should be many new developments in antibiotics and while they may some day be synthesised, there is as yet no development that would seem to offer serious threat of competition to the fermentation product.

Thus it seems evident the production of fermentation chemicals from starch has a good chance to continue into the post-war economy on a stable basis, provided there is the proper co-ordination with agriculture and assuming modern processing is employed, backed by active research into better methods. In the following sections the accomplishments of recent research on processing methods are described. They have as yet been applied only partially in a few plants. Application is still lagging far behind the current research programmes, a most unhealthy situation that must not continue.

The Manufacture of Ethyl Alcohol.—Because the manufacture of ethyl alcohol from grains and other starchy substrates is probably the oldest of the organic chemical industries, it has been rather commonly regarded as near its maximum in efficiency and economy. Beresford and Christensen,¹³ Willkie and Kolochov¹⁷ and Christensen¹⁹ have shown that this is not the case; there are several highly inefficient steps in the orthodox procedure.

The present methods for converting starch to fermentable sugars are especially unsatisfactory. In orthodox processing, 1 part of ground grain and 5 to 6 parts of water, by weight, are mixed in a cooker. Sometimes 0.01 to 0.02 parts of malt are added to provide some precooking liquefaction. The mash is then cooked with direct steam injection and mechanical agitation. Various combinations of time and temperature are used, varying from one hour at 100° C. (212° F.) to 15 minutes at temperatures ranging up to 150° C. (302° F.). More recently continuous pipe cookers have been used in which 5 minutes of cooking at 160° C. (320° F.) or even higher temperatures are used. The temperature of the cooked mash is reduced to substantially 100° C. (212° F.) by blowing down, then to 60° C. (140° F.) by vacuum evaporation. Malt is then added, to the extent of 0.10 to 0.12 parts, usually as a slurry at 63° C. (145° F.) and the mash is held 45 to 60 minutes at that temperature. The mash is then cooled to 27° C. (80° F.) by use of a jacketed cooler, thin stillage is added to adjust the reaction to pH 5.0 to 5.5 and the mash is placed in the fermenter and inoculated with yeast.

The most obvious fault in this process is the high cost and low efficiency of the amylase employed. It is customary to use 8 to 10 parts of barley malt, costing at least 2 cents per pound more than grain, with 92 to 90 parts of grain. When grain costs 1 cent per pound, and the ethanol yield is 31.5 pounds per 100 pounds, the amylases cost 0.63 cents per pound of ethanol, or 20 per cent. of the normal selling price. The ethanol yield obtained is normally less than 85 per cent. of that theoretically possible.

Just before World War I there was a great deal of interest in the use of fungal amylases in place of malt. The amylo process, which has been very well described by Grove²⁰ and by Owen²¹, obtains saccharification by growing certain species of *Mucor* or *Rhizopus* in the grain mash at 35° C. (95° F.) prior to inoculation with yeast. The mould grows submerged and very adequate aeration is required. The yeast used is frequently of the Anamite type because it is able to function at higher temperatures than can the ordinary distillers' yeasts. Ethanol yields reported vary from 33 to 36 pounds per 100 pounds of moisture-free grain, 7 to 12 per cent. better than those obtained with malt saccharification.

But there are some difficulties inherent in the amylo process. First, it is necessary to cool a mash which becomes very viscous as the temperature is reduced unless low mash concentrations are used. Second, a very long incubation period is required, with consequent contamination hazards. Third, it is somewhat difficult to get uniform mould growth, especially in large fermenters. For

these reasons, the amylo process has not found wide application.

Acid saccharification has been quite thoroughly investigated in many commercial plants. Severson²² published the results of a study of the acid saccharification of the starches of several grains. The data are conclusive in showing that acid saccharification alone is inadequate. If conditions of time, temperature and acid concentration are such that there is a minimum of unfermentable dextrins, some of the dextrose is repolymerised to carbohydrates not fermentable, with the result that alcohol yields are generally only about 75 per cent. of those theoretically possible. Acid liquefaction or dextrinisation followed by enzyme saccharification is highly satisfactory, as will be described later, but the amylase requirement is the same as though the acid treatment had not been applied.²³ Thus the development of low cost and highly efficient amylases is still necessary.

Two amylase preparations have been developed that avoid the difficulties inherent in the amylo process and still have the virtue of low cost and high efficiency. Underkofler, Fulmer and Schoene,²⁴ Hao, Fulmer and Underkofler,²⁵ Underkofler,²⁶ Underkofler and Fulmer,²⁷ and Beresford and Christensen¹⁴ have described a fungal amylase (mould bran) made by growing *Aspergillus oryzae* or other moulds on wheat bran and similar fibrous substrates. Beckford, Kneen and Lewis²⁸ have described a bacterial amylase made by growing a selected species of the *subtilis mesentericus* group on wheat bran or other suitable media. The bacteria selected are unlike those used in making present commercial bacterial amylase preparations in that the new material converts substantially 90 per cent. of the starch to fermentable sugars, whereas present commercial bacterial amylases rarely give more than 30 per cent. conversion.

Beresford and Christensen¹⁴ and Christensen¹⁹ point out another serious inefficiency in orthodox processing. On the assumption that each $C_6H_{10}O_5$ unit yields 2 moles of ethanol and 1 of carbon dioxide, 1 pound of ethanol represents 1.761 pounds of original starch. Then since all of the grain not converted to alcohol and carbon dioxide should be recoverable as dry residual solids, the weight of residual solids, plus 1.761 times the weight of ethanol, should equal the weight of grain entering the process, the calculation being made on a moisture-free basis, of course. In commercial operations a yield of 31.5 pounds of ethanol and 23.6 pounds of residual solids from 100 pounds of grain, all moisture-free basis, is considered good. But this accounts for

$$(31.5 \times 1.761) + 23.6 = 81.5 \text{ pounds of grain}$$

That is, during the processing 16·5 pounds of the raw material is lost. Analysis of grain entering the process and of residual solids shows that this loss occurs in the carbohydrate; all the other components are fully accounted for, but only about 75 to 80 per cent. of the carbohydrate of the original grain can be accounted for by alcohol, carbon dioxide and carbohydrate in the residual solids.

This carbohydrate loss has been found to result from a kind of starch retrogradation that occurs during the cooling of the cooked mash. The change is largely irreversible and starts as the cooling mash reaches a temperature of 78° C. (172° F.). Evidence of this has been found in the X-ray diffraction pattern, by viscosity measurements and in fermentation studies, but little is known of its character. However, it is clearly established that the starch undergoing this change is not converted to alcohol by action of yeast but yields weak acids that subsequently, during drying of the residual solids, are converted to carbon dioxide and water, by successive oxidation and decarboxylation. With potatoes the loss may reach 35 per cent. of the starch, whereas not more than 20 per cent. of grain starches is lost.

Four ways of avoiding or minimising this loss of starch have been developed. Christensen²⁹ described an instantaneous cooling process, by which the mash is cooled by dilution with a cold amylase slurry of proper temperature, volume and concentration. Christensen and Taylor³⁰ described a multi-stage amylase addition, the first addition being made above 78° C. (172° F.) and the second after the mash has been cooled to 55° C. to 60° C. (131° F. to 140° F.). Christensen²³ described a combination of cooking at acid reaction such that about 8 per cent. of the starch is converted to fermentable sugars, followed by the addition of fungal amylases. Severson, Kneen and Lewis³¹ described a pre-cooking treatment of the mash with bacterial amylase to split the starch to non-retrograding types, followed by cooking and final saccharification with fungal amylases.

The most generally useful of the mashing and saccharification procedures involves preparation of a mash slurry containing 1 part ground grain, 0·12 parts of the bacterial bran of Beckford, Kneen and Lewis²⁸ and 2 parts water, at a temperature of 55° C. (131° F.) and a reaction of pH 5·5 to 6·0. This is held 10 minutes at 55° C. (131° F.) and then heated at such a rate that in 20 minutes the temperature is 85° C. (185° F.). Then the mash is cooked in a continuous cooker, 10 minutes at 125° C. to 150° C. (257° F. to 302° F.), depending upon the grain used, and cooled by evaporation to 78° C. to 80° C. (172° F. to 176° F.). Then it is quickly

and thoroughly mixed with a cold slurry of mould bran containing 0.025 to 0.035 parts of mould bran in 2 parts of cold water. The temperature of the mixture should not exceed 60° C. (140° F.). After retention for 10 minutes at this temperature, the mash is cooled to 27° C. (80° F.) and inoculated with yeast. It is desirable to adjust the reaction of pH 5.0 to 5.5 when the mould bran slurry and mash are mixed.

This process yields about 15 per cent. more alcohol than can be obtained with present orthodox processing. Typically, 100 pounds of maize or sorghum grains dry basis, yields 37.0 pounds of ethanol and 34.5 pounds of residual solids, dry basis. Then the products represent

$$(37.0 \times 1.761) + 34.5 = 99.6 \text{ pounds of original grain.}$$

This process yields 4.0 to 4.5 pounds more ethanol and 7 to 8 pounds more dry residual solids per 100 pounds of dry grain than does the commonly employed process; the charge for amylase is greatly reduced; and the cost of steam, water, power and other plant operating items is reduced.

N-Butyl Alcohol and Acetone.—In the period just before the first World War an intensive interest in the production of synthetic rubber led to the establishment of plants at Rainham and at King's Lynn by the firm of Strange and Graham, Ltd., for the commercial production of n-butyl alcohol and acetone by the fermentation of potatoes, using a process developed by Fernbach of the Pasteur Institute. The butyl alcohol was to be used as a source of butadiene for the manufacture of synthetic rubber by the Matthews sodium polymerisation process. The history of this industrial programme has been described by Perkin.³²

Immediately after the war started in 1914, the British Admiralty was faced with a serious shortage of acetone for cordite manufacture and later for aeroplane dopes. The principal source of acetone at that time was the wood distillation industry in the United States and Canada, and this industry could not begin to meet the demand. Attention was called to the plants of Strange and Graham which were producing small quantities of acetone from cull potatoes, and under Government contract attempts were made to increase the production of acetone from these plants. The supply of cull potatoes in England was small and Weizmann, in 1915, suggested the use of maize and other grains containing starch. With Weizmann in charge, and with maize and damaged rice as the source of starch, the new process worked very well.³³ Horse-chestnuts were also used to a limited extent.^{34, 35}

Due to easier availability of raw materials, a Toronto grain distillery was remodelled to make butyl alcohol and acetone from maize. After the United States entered the war a distillery at Terre Haute, Indiana, was converted to the same use. With the termination of the war the plants in England, Canada and the United States were closed because acetone was no longer needed in large quantities and butyl alcohol was not in much demand, in fact large stores of the latter had been built up at Toronto and Terre Haute during the period of the war-time operations.

It was not long, however, before a large demand developed for n-butyl alcohol for the manufacture of n-butyl acetate for use in the new automobile lacquers. An American corporation acquired the Weizmann patents³⁶⁻⁴² on a world-wide basis, purchased the Terre Haute Plant, and later constructed a new and much larger plant at Peoria, Illinois, and also plants in England and France. The development and operation of this fermentation industry has been described by Killeffer,⁴³ Gabriel,⁴⁴ Gabriel and Crawford⁴⁵ and Wynkoop.⁴⁶ As a result of extensive research a comprehensive patent structure was built up by this corporation; a few of these patents are listed in the references.⁴⁷⁻⁶¹ Since the expiration of the basic patents and the discovery of new organisms capable of producing n-butyl alcohol and acetone from sugars, at least two other firms in the United States and one in the West Indies have entered the field of butyl alcohol and acetone production by fermentation.

Throughout the years maize has continued to be the basic raw material for the butyl alcohol-acetone fermentation, although other starchy grains have also been employed. The bacteria used, strains of the species now commonly known as *Clostridium acetobutylicum*, produce an amylase that permits the use of starchy substrates directly, without the saccharification step which is needed in the ethanol fermentation. One of the principal disadvantages of the butyl alcohol-acetone fermentation is the low mash concentration that must be employed. The original mash contains 6 to 8 per cent. maize, and a final concentration of 'total solvents' (butyl alcohol, acetone and ethyl alcohol) of 2.2 to 2.5 g. per 100 ml. is about the maximum that can practically be obtained. A high steam consumption is the inevitable result of the low mash concentration for the cooking of the mash, the distillation of the 'solvents' and the recovery of the residual solids.

The commercial method for the production of butyl alcohol and acetone from maize involves mixing the ground grain meal with water to give a concentration of 6 to 8 per cent. solids, cooking the mixture under steam pressure, which gelatinises the starch

and sterilises the mash, pumping the cooked mash aseptically through coolers where the temperature is reduced to about 37° C. into the covered fermenters, inoculating with plant cultures of *Cl. acetobutylicum*, and allowing to ferment for 48 to 72 hours. It is essential to sterilise all the fermenters, pipes and equipment with which the mash or butanol organisms may come into contact for contamination in this fermentation is a very serious matter. The 'solvents' are recovered at the end of the fermentation by distillation.

The yield of 'total solvents' from maize varies in practice from 26 to 28 g. from 100 g. of dry matter in the maize used, or about 36 to 39 g. from 100 g. of starch. Normally the 'total solvents' consist of 60 to 62 per cent. of n-butyl alcohol, 29 to 31 per cent. of acetone and 8 to 11 per cent. of ethyl alcohol by weight. The gases produced during fermentation, carbon dioxide and hydrogen, amount to more than 1.5 times the weight of neutral solvents produced.

The development of inoculum or seed cultures of *Cl. acetobutylicum* has been an object of much investigation since continued transfer in maize mash results in the culture becoming sluggish. For plant use cultures of the organism are allowed to sporulate and the spores are stored in the dry condition on soil or sand. For the inoculation of plant fermenters, the culture is started in the laboratory from these stock spore cultures, and built up through daily transfer to fresh sterile maize medium in increasing volume. The 5th to 7th such transferal is made into the fermenter, the 'solvent' yielding ability being at a maximum at that stage.

On occasions it has been observed in practice that, although the fermentations start normally, the acidity fails to decrease ('break') and the fermentations end abruptly leaving a large amount of residual carbohydrate with the formation of acetic and butyric acids, and a low yield of 'solvents'. Legg^{49,50} described the causative factor of this so-called 'sluggish' condition, as a filtrable, reproducing, thermolabile one, resembling a bacteriophage in some respects, and described a technique of acclimatising or of selecting an immune strain. Starr⁶² further described the effect and confirmed the work of Legg. Starr also showed that the filtrate did not produce lysis or otherwise induce changes in morphology, but that it did affect the metabolic processes of the butyl alcohol bacteria.

For many years investigators have attempted to adapt the butyl-alcohol-acetone fermentation to use other raw materials than grain starch, such as blackstrap molasses or hydrolysates

from agricultural wastes. Underkoffler, Christensen and Fulmer,⁶³ and Underkoffler, Fulmer and Rayman⁶⁴ have shown experimentally that as much as 80 per cent. of corn meal may be replaced by sucrose or glucose without sacrificing high yields. Xylose may replace maize meal to the extent of 40 or 50 per cent. Thus it is possible to ferment, along with maize meal, cheap materials which would, by themselves, be fermented poorly. Although no commercial application has resulted as yet, this is a sound practice from the point of view of conservation and economics. Recent developments in the saccharification of agricultural residues⁶⁵ may lead to future expansion in this field.

Until about 1935, attempts to use blackstrap molasses as the sole raw material instead of grain for the butyl alcohol-acetone fermentation with *Cl. acetobutylicum* were unsuccessful. However, other bacteria have been discovered⁶⁶⁻⁷⁷ which ferment molasses well, and for several years molasses was the principal raw material for this fermentation industry in several plants in the United States and the West Indies. In 1942, molasses became unavailable in the United States, as mentioned above, and the butyl alcohol-acetone fermentation industry again turned to the use of grains.

Both n-butyl alcohol and acetone are now made synthetically, but the fermentation industry had been able to meet this competition and as additional by-products are developed the economic status of the fermentation process is improved. At present, methyl alcohol is made from the hydrogen and carbon dioxide produced in the fermentation, and pure riboflavin, riboflavin concentrates, vitamin concentrated and livestock feed are made from the stillage.

Glycerol.—The production of glycerol by yeasts in small amounts, up to 3·5 per cent. of the weight of sugar fermented, as a normal by-product in alcohol fermentation, was first noted by Pasteur. Although means of improving the yields of glycerol have been developed there has not been a large commercial production of glycerol by this process, except in Germany during the first World War, because of the high cost of materials used and of the recovery of the glycerol from the fermentation mixture. There is at present considerable interest in the production of glycerol by new methods, particularly in the United States, since the yield from soap manufacture has been unable to keep pace with the increasing demand for the product, even in peacetime.

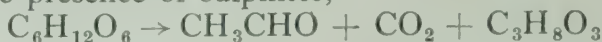
About three years before the beginning of the first World War Neuberg and his co-workers began to publish some of the results of their studies concerning the mechanism of the ethyl alcohol

fermentation by yeasts.^{78,79} Three general courses for the fermentation of sugars by yeast were described:

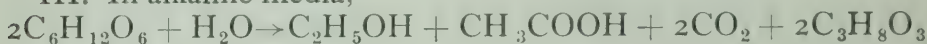
I. Normal, in acid media,



II. In the presence of sulphites,



III. In alkaline media,



Connstein and Ludecke^{80,81} developed the German process which was employed in that country during the first World War. In this sulphite process beet sugar was used along with large amounts of sodium sulphite. Cocking and Lilly^{82,83} developed a process in England in which a mixture of sulphite and bisulphite were used. In the United States an alkaline process was developed by Eoff.⁸⁴ Details of these processes have been reported by Eoff, Linder and Beyer,⁸⁵ Ling,⁸⁶ May and Herrick⁸⁷ and Nord.⁸⁸ Each of these processes depends upon altering the course of the normal ethyl alcohol fermentation, the addition of sulphites changing it in accordance with Equation II above and the addition of alkalis in accordance with Equation III. This change is not complete however, and to a certain degree the normal alcoholic fermentation continues. The theoretical yield of glycerol is 51 g. per 100 g. of hexose. The alkaline process gives yields of 10 to 15 g. of glycerol per 100 g. of sugar, and large amounts of alkali are required. The sulphite process yields about 35 g. of glycerol per 100 g. of sugar and requires an amount of sodium sulphite equal to or greater than the weight of sugar initially present in the medium.

The very large amounts of soluble salts present after the completion of the glycerol fermentations renders the recovery of the product very difficult. A low percentage of the glycerol present is recoverable, the quality is poor and the cost of recovery is high. These factors, along with the cost of the large amounts of alkali or sulphite used, prevent the commercial utilisation of the above mentioned glycerol fermentation processes in normal times.

Research for the development of a glycerol fermentation process better suited to commercial application has resulted in a procedure involving the use of slightly soluble sulphites instead of sodium sulphite. Calcium or magnesium sulphites are employed, and the medium is controlled at a slightly acid reaction to provide the optimum bisulphite concentration. At the end of the fermentation, excess sulphite is filtered off along with the yeast, the ethyl alcohol and the acetaldehyde, released from the soluble bisulphite complex,

are recovered by distillation, and the residual liquid furnishes a relatively salt-free material from which the glycerol may be recovered. This process is covered by a U.S. patent application⁸⁹ which has been allowed and will soon issue, and was developed for use with sugar solutions or molasses. Pilot plant operations leading to possible full plant scale operations were underway when molasses became unavailable in the United States in 1942. Some attempt was made to adapt the process to malted grain mash, but the results were unfavourable and this work was abandoned. It is probable the process could be used with acid hydrolysed starch syrups, particularly if mould amylase were also employed for conversion of residual dextrins in the syrups.

Lactic Acid.—Apparently Avery, of Littleton, Massachusetts, first successfully produced lactic acid by fermentation on a commercial basis in 1881. However, until recently, the lactic acid industry was largely centred in Europe. Dark lactic acid has long been used for deliming hides and in the plumping and bating of leathers. The light edible grades have had a limited use in the production of food products. Within recent years additional uses for lactic acid, metal lactates, and the ethers and esters of lactic acid have been discovered.⁹⁰ Currently there is a great interest in lactic acid or aliphatic lactates as a source of acrylate plastics,⁹¹⁻⁹⁶ and this has given a decided impetus to research on the commercial development of the lactic acid fermentation industry.

Lactic acid is produced commercially in the United States to a limited extent by fermentation of by-product casein whey^{97, 98} or of molasses. By far the major portion, however, is derived from the relatively high temperature fermentation of acid-saccharified starch. In Germany potato starch and in the United States maize starch are the usual substrates. Peckham⁹⁹ has recently reviewed the commercial manufacture of lactic acid.

At present the customary method in the United States is to use as the substrate a starch-rich fraction from maize-milling, and to saccharify it by cooking with a dilute mineral acid, sometimes following this procedure with the addition of an amylase. Accessory growth factors are required by lactic acid bacteria, and these are commonly supplied by addition of malt sprouts or steep-water. Mould bran has recently been found to be a still more advantageous source of the necessary growth factors and markedly reduces the time required for completion of the fermentation. The resulting medium containing 5 to 20 per cent. of sugars, is inoculated with a suitable culture of lactic acid organisms, commonly *Lactobacillus delbrückii* or *Lactobacillus bulgaricus*, and the

fermentation allowed to proceed at 50° C. The lactic acid formed must be neutralised in order that the fermentation will go to completion. Calcium or zinc carbonate or hydroxide may be added either at the beginning or intermittently as the fermentation progresses. The advantage of adding the neutralising agent intermittently lies in the fact that an acid reaction helps to prevent contamination.

The dark, crude or commercial grades of lactic acid are prepared from the final fermentation liquors by adding sulphuric acid exactly equivalent to the calcium present, filtering and concentrating to the desired strength in vacuum evaporators. The water-white, plastics, edible and U.S.P. grades are prepared in a number of ways. Smith and Claborn¹⁰⁰ have briefly discussed six methods for accomplishing the purification of lactic acid. The preferred method⁹⁹ for obtaining the purest lactic acid commercially is through the methyl ester. Lactic acid or sodium or calcium lactate is first dehydrated and then esterified with methyl alcohol. The methyl lactate is separated by careful fractional distillation and the ester hydrolysed by boiling with an excess of water. The methyl alcohol is then removed by distillation and the lactic acid concentrated in vacuum evaporators. A second method involves extraction of the lactic acid from the crude aqueous solution by means of a suitable immiscible solvent. One application of this process is described in detail by Jene-mann,¹⁰¹ isopropyl ether being employed as the extractant. A third method¹⁰⁰ involves crystallisation of zinc lactate, purification by repeated re-crystallisation, the liberation of the acid from the zinc lactate in solution by means of hydrogen sulphide, decolorisation with charcoal, and filtration. The filtrate is then concentrated by vacuum evaporation to the required concentration. The oldest method^{99, 100} involves crystallisation of the lactic acid from the fermentation liquors as calcium lactate. The washed, solid, crude calcium lactate is dissolved in hot water, an equivalent amount of sulphuric acid is added to precipitate the calcium, decolorising carbon is then added, the mix agitated thoroughly and the solids removed by vacuum filtration. The filtrate is then concentrated in vacuum evaporating pans.

Certain mixed cultures of thermophilic lactic acid bacteria are known to be able to ferment starchy substrates directly therefore obviating the need for preliminary conversion of the starch, but as far as is known, no commercial application of this process has been made.

Butylene Glycol.—As described above, there was a great deal of interest in 2, 3-butylene glycol as a source of butadiene in the

early days of the synthetic rubber programme. Although the direct catalytic dehydration of 2, 3-butylene glycol to butadiene had not as yet been regularly accomplished with satisfactory yields, the method of Hill and Isaacks¹⁰² for dehydration of the diacetate of the glycol has been successfully demonstrated through the pilot plant scale. Elder¹⁰³ reported that in this manner an overall conversion of 2, 3-butylene glycol to butadiene of at least 88 per cent. of theory has been obtained in a pilot plant.

Butylene glycol, or its partial oxidation products, acetyl-methylcarbinol and diacetyl, have long been known as minor products of several bacterial fermentations of starch and sugars. Two bacteria are of particular interest for this fermentation, *Aerobacter aerogenes* and *Aerobacillus polymyxa*.

Breden and Fulmer¹⁰⁴ and Fulmer, Christensen and Kendall¹⁰⁵ reported extensive studies on methods to improve the production of the glycol by *Aerobacter* from sugars. Kluver and Scheffer¹⁰⁶ patented a method for the commercial production of the glycol. Since *Aerobacter aerogenes* is deficient in amylase, sugars, molasses or saccharified starch mashers are employed as the substrate for this organism. Saccharified whole grain mashers may be used but are not so satisfactory since the residual solids interfere with recovery of the glycol. *Aerobacter aerogenes* produces a product which is principally meso-2, 3-butylene glycol.¹⁰⁷ Small amounts of lactic acid and of ethyl alcohol are also produced in this fermentation.

Aerobacillus polymyxa ferments starchy substrates directly, in fact it does not function well on mashers containing sugars. Grain mashers have commonly been employed as the fermentation substrate^{108, 109} but mashers containing starch with nutrients also give good results, and facilitate recovery of the glycol due to absence of residual solids. The products of the fermentation with *Aerobacillus polymyxa* are butylene glycol and ethyl alcohol in the ratio of approximately 1.5 to 2.0 parts of glycol to 1 part of alcohol, by weight. The glycol produced is the laevo form.¹⁰⁷ The principal disadvantage of this fermentation is the relatively low mash concentration that can be employed.

The butylene glycol may be recovered from the fermented mashers by steam distillation or by extraction with butanol or ethyl ether or other suitable solvent. If extraction is used, which gives better recovery, the fermented mash is concentrated by evaporation to about 20 to 22 per cent. glycol before extraction. The crude glycol is purified by fractional distillation.

Large-scale pilot plant operations in several locations in Canada and the United States have proven the practicability of the 2, 3-

butylene glycol fermentation, using either *Aerobacter aerogenes* or *Aerobacillus polymyxa*, and industrialisation only awaits the development of a demand for the product.

Penicillin and Other Antibiotics.—Antibiotic activity is not a new discovery. In 1877, Pasteur noticed inhibition in the growth of anthrax bacillus by certain air-borne contaminants. Considerable research was devoted to bacterial antagonism around the turn of the century, but no practical applications resulted. In 1929, Alexander Fleming, an English bacteriologist, announced the discovery of a mould which, floating from the air into a plant culture of *Staphylococcus aureus*, formed a green colony and destroyed the bacteria for some distance around it. Other bacteriologists had frequently noted similar phenomena but had not followed up the observations. Fleming found his mould produced a substance which prevented the growth of many common pathogenic bacteria, and since the mould proved to be a species of *Penicillium* he named the new antibacterial substance 'penicillin'. Attempts by Fleming and prominent biochemists to isolate and purify the active substance failed, and penicillin was almost forgotten by everyone, except Fleming.

In 1937, a group of bacteriologists and chemists at Oxford University in England began to re-examine the potentialities of penicillin. They demonstrated that penicillin surpassed the famed sulpha drugs in protective power against many pathogenic organisms, and furthermore that it was almost completely non-toxic to animals. So great was its promise that in 1941 Professor Florey, director of penicillin research at Oxford, was sent to the United States to promote interest in that country.

As the result of co-operative research between governmental, university and industrial research laboratories yields were improved from a maximum of 20 Oxford units per millilitre of medium to 50 units then to 100 and finally to 150 units in surface cultures. Later, strains of *Penicillium* were discovered which allowed the production of penicillin in deep tanks, first giving yields of 50 units per millilitre, and finally up to 250 units as culture media and deep-culture equipment were improved. Tens of thousands of strains of *Penicillium* have been tested for penicillin-producing power, and other thousands of variants have also been tested. From all these a score of high-yielding strains have been sorted, the yields from some of which are almost certain to be higher than those obtained with Fleming's *Penicillium notatum*. The vast amount of co-operative research in the various laboratories in the United States has been co-ordinated by Dr. R. D. Coghill and his associates of the Fermentation Division of the

Northern Regional Research Laboratory of the United States Department of Agriculture, Peoria, Illinois. Coghill¹¹⁰ has published a review of some of this co-operative work.

Three methods of cultivation of the moulds for penicillin production have been used for commercial production of this antibiotic: (a) shallow surface cultures of the moulds on liquid nutrient medium in bottles; (b) deep submerged culture, in which the organism growing throughout liquid medium of any depth is artificially supplied with air forced through the medium from the bottom of the vessel; and (c) growth of the mould on moist sterile bran, each particle of bran offering its whole surface as a substrate for growth. Technical difficulties encountered in the use of this latter type of culture on bran have led to its abandonment; but for the production of mould spores to be used as seed with which to inoculate surface and submerged cultures on a large scale, bran cultures are unexcelled. The major part of present commercial production of penicillin employs the deep-culture method, the medium used containing dextrose, obtained from starch, maize steep liquor and other nutrients. When the penicillin content has reached a maximum the penicillin is recovered from the filtrate after removing the mould by adsorption and solvent extraction. The sodium salt is then prepared and dried in low temperature vacuum driers.

Antibiotics from many other micro-organisms have also been prepared. A few examples include, from *Aspergillus* species flavicidin or flavicin¹¹¹⁻¹¹³ (perhaps identical with penicillin) and clavacin¹¹⁴⁻¹¹⁶; gramicidin from *Bacillus brevis*^{117, 118}; and streptomycin from *Actinomyces griseus*.¹¹⁹ So far none of these other antibiotics has proven as generally valuable as penicillin, but undoubtedly some will be found useful for specific therapeutic uses and active investigation of them is under way in several laboratories. The potentiality of micro-organisms as a source of chemotherapeutic agents was well expressed by Fleming when he said that it would be remarkable indeed if the first useful mould antibiotic to be discovered should be the last, or even the best.

Other Fermentation Products and Processes.—Through the activities of micro-organisms, employing species of bacteria or moulds, a large number of chemicals may be produced. In some cases these fermentation processes are operated at present on a large industrial scale, in others production is on a relatively small scale, and in still others work has been completed only on the laboratory scale, and these processes await development of industrial demands. In most cases the substrates employed are sugars of various kinds, rather than starch, although dextrose

produced from starch is a common raw material. Likewise, fermentation processes are important in the manufacture of many beverage and food products such as fermented milk products, cheeses, pickles, sauerkraut, etc., the processing of tobacco, and in the retting of fibrous plant stalks for separation of cordage and fibres. A discussion of many of these interesting and important or potentially important processes is not properly a matter for consideration here. However, the more important fermentation processes in which micro-organisms are the causative agents will be briefly considered.

Edible grades of acetic acid (vinegars) are produced from dilute ethyl alcohol solutions by bacterial oxidations by cultures of *Acetobacter*.^{120, 121} *Acetobacter suboxydans* is employed for the production of sorbose, used in the synthesis of ascorbic acid^{122, 123}, and for the production of dihydroxyacetone^{124, 125} as well as a number of other rare sugars. During the first World War considerable work was done on the development of a fermentation process for producing acetone and ethyl alcohol^{126, 127}, but it has never found successful industrial application. Propionic acid may be produced by the fermentation of carbohydrates by propionic acid bacteria. This fermentation has occasioned much research and offers possibilities for future commercial development should sufficient demand for the acid develop¹²⁸⁻¹³⁰.

A number of fermentation processes employing moulds are of immediate importance or promising for future application. Citric acid is prepared on a large industrial scale by the surface culture fermentation of sugars, usually sucrose, with appropriate strains of *Aspergillus niger*^{131, 132}. Gluconic acid is produced, as the calcium salt, by submerged culture fermentation of dextrose (from starch) by a selected strain of *Aspergillus niger*¹³³⁻¹³⁵. Lactic acid, kojic acid, fumaric acid, itaconic acid and many other acids and metabolic substances have been isolated as products of various mould fermentations. A series of more than 70 papers by Prof. Harold Raistrick and his associates has reported the isolation of a large number of metabolic products of many species of moulds. The first 18 papers appeared in the *Philosophical Transactions of the Royal Society of London. Series B*, 1931, 220, 1-367. The others have appeared in the *Biochemical Journal* from 1931 to date. Some of the many products of mould metabolism may in the future become of commercial importance. For instance itaconic acid would seem to have excellent opportunities in the plastics field and research has made possible the ready production of this chemical by a mould fermentation process.¹³⁶

One of the rather spectacular recent developments is the discovery that vitamin B₁₂, first isolated from liver and responsible or at least a large part of the value of liver in the treatment of anaemia, is a by-product in the manufacture of streptomycin. There is great current research activity in this field in connection with B₁₂ and associated compounds that comprise the so-called 'animal protein factor' (APF). It is currently believed that this APF will greatly improve the value of vegetable proteins for livestock feeding and probably also for human food, and thus may profoundly affect world food supplies.

REFERENCES

1. E. I. FULMER and C. H. WERKMAN, *The Chemical Action of Micro-organisms*, Charles C. Thomas, Baltimore, 1930.
2. RUBBER RESERVE COMPANY, *Rept. on the Rubber Program 1940-45*, 1945.
3. E. I. FULMER, *Iowa Corn Res. Inst.*, 1943, **3**, No. 1.
4. U.S. Senate Sub-committee of Committee on Agriculture and Forestry, *77th Congress, S. Res. 224, Hearings*, 1942-43.
5. A. T. COLWELL, R. E. CUMMINGS and D. E. ANDERSON, *Soc. Aut. Engrs. transactions*, January 8, 1945.
6. D. A. HOWES, *The Science of Petroleum*, by Dunstan, Nash, Brooks and Tizard, 1938, Vol. 4, p. 2454, Oxford Uni. Press, London.
7. ALEX TAUB, *Automotive and Aviation Industries*, 1944, July 15.
8. L. T. BROWN and L. M. CHRISTENSEN, *Ind. Eng. Chem.*, 1936, **28**, 650.
9. L. M. CHRISTENSEN, *Ind. Eng. Chem.*, 1936, **28**, 1089.
10. L. M. CHRISTENSEN, *Iowa Corn Res. Inst.*, 1939, **1**, No. 2, 192.
11. P. B. JACOBS and H. P. NEWTON, *U.S. Dept. Agr., Misc. Pub.* 327, 1938.
12. G. SHEPHERD, W. K. MCPHERSON, L. T. BROWN and R. M. HIXON, *Iowa Corn Res. Inst.*, 1940, **1**, No. 3.
13. H. BERESFORD and L. M. CHRISTENSEN, *Idaho Agr. Expt. Sta. Bull.* No. 241, 1941.
14. W. J. HALE, *Farmward March*, Coward-McCann, New York, 1939.
15. L. M. CHRISTENSEN, R. M. HIXON and E. I. FULMER, *Power Alcohol and Farm Relief*, Chemical Foundation, New York, 1934.
16. L. M. CHRISTENSEN, *Chem. Ind.*, 1940, November.
17. H. F. WILLKIE and P. J. KOLACHOV, *Food for Thought*, Indiana Farm Bureau, Indianapolis, 1942.
18. H. C. FILLEY, W. J. LOEFFEL and L. M. CHRISTENSEN, *Nebr. Chemurgy Project Prog. Rept. No. 9*, 1943.
19. L. M. CHRISTENSEN, *Cereal Chem.*, 1943, **20**, 478.
20. OTTO GROVE, *J. Inst. Brew.*, 1914, **20**, 248.
21. W. L. OWEN, *Ind. Eng. Chem.*, 1933, **25**, 87.
22. G. M. SEVERSON, *Iowa State Coll. J. Sci.*, 1937, **11**, 215.
23. L. M. CHRISTENSEN, U.S.P. 2,348,451, 9/5/1944.
24. L. A. UNDERKOFER, E. I. FULMER and L. SCHOENE, *Ind. Eng. Chem.*, 1939, **31**, 734.
25. L. C. HAO, E. I. FULMER and L. A. UNDERKOFER, *Ind. Eng. Chem.*, 1943, **35**, 814.
26. L. A. UNDERKOFER, *Brewers Digest*, 1942, **17**, No. 12, 29.
27. L. A. UNDERKOFER and E. I. FULMER, *Chronica Botanica*, 1943, **7**, 42^c or a
28. L. D. BECKORD, ERIC KNEEN and K. H. LEWIS, *Ind. Eng. Chem.*, 194^c, 692.
29. L. M. CHRISTENSEN, U.S.P. 2,342,330, 22/2/1944.
30. L. M. CHRISTENSEN and G. G. TAYLOR, U.S.P. Application, ^{e method} give thick, 438,842, 13/4/1942.

31. G. M. SEVENSON, ERIC KNEEN and KEITH H. LEWIS, Unpublished data, 1944.
32. W. H. PERKIN, *J. Soc. Chem. Ind.*, 1912, **31**, 616.
33. A. GILL, *J. Soc. Chem. Ind.*, 1919, **38**, 273T.
34. F. NATHAN, *J. Soc. Chem. Ind.*, 1919, **38**, 271T.
35. A. GILL, *J. Soc. Chem. Ind.*, 1919, **38**, 411T.
36. C. WEIZMANN, E.P. 4845, 29/3/1915.
37. C. WEIZMANN, E.P. 149,355, 24/2/1916.
38. C. WEIZMANN, E.P. 150,360, 25/5/1917.
39. C. WEIZMANN, U.S.P. 1,315,585, 9/9/1919.
40. C. WEIZMANN, U.S.P. 1,437,677, 5/12/1922.
41. C. WEIZMANN and G. A. HAMMLYN, U.S.P. 1,329,214, 27/1/1920.
42. C. WEIZMANN and H. M. SPIERS, E.P. 164,762, 3/1/1919.
43. D. H. KILLEFFER, *Ind. Eng. Chem.*, 1927, **19**, 46.
44. C. L. GABRIEL, *Ind. Eng. Chem.*, 1928, **20**, 1063.
45. C. L. GABRIEL and F. M. CRAWFORD, *Ind. Eng. Chem.*, 1930, **22**, 1163.
46. R. WYNKOOP, *Ind. Eng. Chem.*, 1943, **35**, 1240.
47. D. A. LEGG, E.P. 278,307, 1/10/1926.
48. D. A. LEGG, U.S.P. 1,582,408, 27/4/1926.
49. D. A. LEGG, U.S.P. 1,668,814, 8/5/1928.
50. D. A. LEGG, U.S.P. 1,911,174, 23/5/1933.
51. D. A. LEGG, U.S.P. 1,927,814, 19/9/1933.
52. D. A. LEGG, U.S.P. 2,023,368, 3/12/1935.
53. D. A. LEGG and L. M. CHRISTENSEN, U.S.P. 1,913,164, 6/6/1933.
54. D. A. LEGG and M. T. WALTON, U.S.P. 2,132,358, 4/10/1938.
55. W. N. McCUTCHAN and C. F. ARZBERGER, U.S.P. 2,023,087, 3/12/1935.
56. E. RICARD, U.S.P. 1,385,888, 1921.
57. E. RICARD, U.S.P. 1,550,746, 25/8/1925.
58. H. R. STILES, U.S.P. 2,023,374, 3/12/1935.
59. H. R. STILES, U.S.P. 2,098,200, 2/11/1937.
60. H. R. STILES and P. W. WILSON, U.S.P. 1,932,755, 31/10/1933.
61. J. C. WOODRUFF, H. R. STILES and D. A. LEGG, U.S.P. 2,089,522, 10/8/1937.
62. D. F. STARR, Thesis, Iowa State College, Ames, 1933.
63. L. A. UNDERKOFER, L. M. CHRISTENSEN and E. I. FULMER, *Ind. Eng. Chem.*, 1936, **28**, 350.
64. L. A. UNDERKOFER, E. I. FULMER and M. M. RAYMAN, *Ind. Eng. Chem.*, 1937, **29**, 1290.
65. J. W. DUNNING and E. C. LATHROP, *Ind. Eng. Chem.*, 1945, **37**, 24.
66. C. F. ARZBERGER, U.S.P. 2,050,219, 4/8/1936.
67. C. F. ARZBERGER, U.S.P. 2,139,108, 6/12/1938.
68. H. E. HALL, U.S.P. 2,147,487, 14/2/1939.
69. F. M. HILDEBRANDT and N. M. ERB, U.S.P. 2,169,246, 15/8/1939.
70. A. IZSAK and F. J. FUNK, U.S.P. 1,908,361, 9/5/1933.
71. D. A. LEGG and H. R. STILES, U.S.P. 2,089,562, 10/8/1937.
72. J. F. LOUGHLIN, Can.P. 335,813, 19/9/1933.
73. J. F. LOUGHLIN, U.S.P. 1,992,921, 26/2/1935.
74. J. F. LOUGHLIN, Ger.P. 629,694, 18/5/1936.
75. E. F. MCCOY, U.S.P. 2,110,109, 1/3/1938.
76. J. M. SHERMAN and N. M. ERB, U.S.P. 2,017,572, 15/10/1935.
77. A. O. SMITH CORP., French P. 742,206, 30/7/1932.
78. C. NEUBERG and A. HILDESCHMEIER, *Biochem. Zeit.*, 1911, **31**, 170.
79. C. NEUBERG and E. REINFURTH, *Biochem. Zeit.*, 1920, **106**, 281.
80. W. CONNSTEIN and W. LUDECKE, G.P. 298,593-298,596, 1915.
81. W. CONNSTEIN and W. LUDECKE, U.S.P. 1,511,754, 14/10/1924.
82. A. T. COCKING and C. H. LILLY, E.P. 164,034, 1921.
83. A. T. COCKING and C. H. LILLY, U.S.P. 1,425,838, 15/8/1922.
84. W. V. LINDER and G. F. BEYER, *Ind. Eng. Chem.*, 1919, **11**, 842.
85. A. T. COCKING, *J. Soc. Chem. Ind.*, 1919, **38**, 175.
86. A. T. COCKING and H. T. HERRICK, *Ind. Eng. Chem.*, 1930, **22**, 1172.

88. F. F. NORD, *Chem. Rev.*, 1940, **26**, 423.
89. R. J. HICKEY, E. I. FULMER and L. A. UNDERKOFER, U.S. Patent Application.
90. L. T. SMITH and H. V. CLABORN, *Ind. Eng. Chem. (News Ed.)*, 1939, **17**, 370.
91. H. V. CLABORN and L. T. SMITH, *J. Am. Chem. Soc.*, 1939, **61**, 2727.
92. L. T. SMITH and H. V. CLABORN, *Ind. Eng. Chem.*, 1940, **32**, 692.
93. L. T. SMITH, C. H. FISHER, W. P. RATCHFORD and M. L. FEIN, *Ind. Eng. Chem.*, 1942, **34**, 473.
94. W. C. MAST, L. T. SMITH and C. H. FISHER, *Ind. Eng. Chem.*, 1945, **37**, 365.
95. W. P. RATCHFORD and C. H. FISHER, *Ind. Eng. Chem.*, 1945, **37**, 382.
96. E. M. FILACHIONE, J. H. LENGEL and C. H. FISHER, *Ind. Eng. Chem.*, 1945, **37**, 388.
97. L. V. BURTON, *Food Industries*, 1937, **9**, 571, 617, 634.
98. T. R. OLIVE, *Chem. and Met. Eng.*, 1936, **43**, 480.
99. G. T. PECKHAM, *Chem. & Eng. News (ACS)*, 1944, **22**, 440.
100. L. T. SMITH and H. V. CLABORN, *Ind. Eng. Chem. (News Ed.)*, 1939, **17**, 641.
101. J. A. JENEMANN, U.S.P. 1,906,068, 25/4/1933.
102. R. HILL and E. ISAACKS, U.S.P. 2,224,912 17/12/1940.
103. A. L. ELDER, *Ind. Eng. Chem.*, 1942, **34**, 1260.
104. C. R. BREDEN and E. I. FULMER, *Iowa State Coll. J. Sci.*, 1931, **5**, 133.
105. E. I. FULMER, L. M. CHRISTENSEN and A. R. KENDALL, *Ind. Eng. Chem.*, 1933, **25**, 798.
106. A. J. KLUYVER and C. SCHEFFER, U.S.P. 1,899,156, 28/2/1933.
107. G. E. WARD, O. G. PETTIJOHN, L. B. LOCKWOOD, and R. D. COGHILL, *J. Am. Chem. Soc.*, 1944, **66**, 541.
108. H. KATZNELSON, *Can. J. Research*, 1944, **22c**, 235.
109. G. A. LEDINGHAM and G. A. ADAMS, *Can. Chem. Process Inds.*, 1944, **28**, 742,801.
110. R. D. COGHILL, *Chem. & Eng. News (ACS)*, 1944, **22**, 588.
111. C. M. MCKEE, G. RAKE and C. L. HOUCK, *J. Bact.*, 1944, **47**, 187.
112. M. T. BUSH and A. GOTH, *J. Pharm. Exp. Ther.*, 1943, **78(2)**, 164.
113. S. A. WAKSMAN and E. BUGIE, *Proc. Natl. Acad. Sci.*, 1943, **29**, 282.
114. B. P. WEISNER, *Nature*, 1942, **149**, 356.
115. S. A. WAKSMAN, E. S. HORNING and E. L. SPENCER, *Science*, 1942, **96**, 202.
116. S. A. WAKSMAN and A. SCHATZ, *Proc. Natl. Acad. Sci.*, 1943, **29**, 74.
117. R. J. DUBOS, *J. Exptl. Med.*, 1939, **70**, 1.
118. G. F. GAUZE and M. G. BRAZHNKOVA, *Am. Rev. Soviet Med.*, 1944, **2**, 134.
119. A. SCHATZ and S. A. WAKSMAN, *Proc. Soc. Exptl. Biol. Med.*, 1944, **57**, 244.
120. W. R. FETZER, *Food Industries*, 1930, **2**, 489.
121. A. E. HANSEN, *Food Industries*, 1935, **7**, 277.
122. E. I. FULMER, J. W. DUNNING, J. F. GUYMON, and L. A. UNDERKOFER, *J. Am. Chem. Soc.*, 1936, **58**, 1012.
123. P. A. WELLS, L. B. LOCKWOOD, J. J. STUBBS, E. T. ROE, N. PORGES and E. A. GASTROCK, *Ind. Eng. Chem.*, 1939, **31**, 1518.
124. C. NEUBERG and E. HOFMAN, *Biochem. Zeit.*, 1935, **279**, 318.
125. L. A. UNDERKOFER and E. I. FULMER, *J. Am. Chem. Soc.*, 1937, **59**, 301.
126. J. H. NORTHRUP, L. H. ASHE and J. K. SENIOR, *J. Biol. Chem.*, 1919, **39**, 1.
127. E. B. FRED, W. H. PETERSON and J. A. ANDERSON, *Ind. Eng. Chem.*, 1923, **15**, 126.
128. E. O. WHITTIER and J. M. SHERMAN, *Ind. Eng. Chem.*, 1923, **15**, 729.
129. C. H. WERKMAN, R. M. HIXON, E. I. FULMER and C. N. RAYBURN, *P. in Iowa Acad. Sci.*, 1929, **36**, 111.
130. P. W. WILSON, U.S.P. 1,898,329, 21/2/1933.
131. F. CHALLENGER, *Ind. Chemist*, 1929, **5**, 181.
132. P. A. WELLS and H. T. HERRICK, *Ind. Eng. Chem.*, 1938, **30**, 255e method
133. P. A. WELLS, A. J. MOYER, J. J. STUBBS, H. T. HERRICK and give thick, *Ind. Eng. Chem.*, 1937, **29**, 653.

134. A. J. MOYER, P. A. WELLS, J. J. STUBBS, H. T. HERRICK, and O. E. MAY, *Ind. Eng. Chem.*, 1937, **29**, 777.
 135. A. J. MOYER, E. J. UMBERGER and J. J. STUBBS, *Ind. Eng. Chem.*, 1940, **32**, 1379.
 136. L. B. LOCKWOOD and G. E. WARD, *Ind. Eng. Chem.*, 1945, **37**, 405.

ADDITIONAL REFERENCES

- R. BAETSLE, *Bull. assoc. elevés inst. super. fermentations Gand.*, 1938, **31**, 274. (Preparation of lactic acid by fermentation.)
 K. BERNHAUER, *Gärungschemisches Praktikum*, 2nd ed., Verlag Julius Springer, Berlin, 1939. (Discusses theoretical and practical aspects of all types of fermentations.)
 J. H. BIRKINSHAW, *Biol. Rev. Cambridge Phil. Soc.*, 1937, **12**, 357. (Biochemistry of the lower fungi.)
 K. R. BUTLIN, *Chemistry Research, Special Rept.*, **2**, H.M. Stationery Office, London, 1936. (Biochemical activities of the acetic acid bacteria.)
 F. CHALLENGER, *Ind. Chemist*, 1930, **61**, 97. (Some fermentative changes of technical interest.)
 I. CHRZASZCZ and J. JANICKI, *Chem. and Ind.*, 1936, **55**, 884. (Recent advances in the fermentation industries.)
 P. W. CLUTTERBUCK, *J. Soc. Chem. Ind.*, 1936, **55**, 551. (Recent developments in the biochemistry of molds.)
 C. N. FREY, *Ind. Eng. Chem.*, 1930, **22**, 1154. (History and development of the modern yeast industry.)
 C. N. FREY, G. W. KIRBY and A. SCHULTZ, *Ind. Eng. Chem.*, 1936, **28**, 879. (Yeast: physiology, manufacture and uses.)
 E. I. FULMER, *Ind. Eng. Chem.*, 1930, **22**, 1148. (The chemical approach to problems of fermentation.)
 E. I. FULMER, *Brewers Digest*, August and September, 1943. (Review of fermentative activities of micro-organisms.)
 A. JÖRGENSEN, *Practical Management of Pure Yeast*, 3rd ed., revised by A. Hansen, Charles Griffin & Co., London, 1936.
 L. B. LOCKWOOD and A. J. MOYER, *Botan. Rev.*, 1938, **4**, 140. (Production of chemicals by filamentous fungi.)
 O. E. MAY and H. T. HERRICK, *U.S. Dept. Agr., Circ.* 216, 1932. (Production of organic acids from carbohydrates by fermentation.)
 O. L. OSBURN and C. H. WERKMAN, *Ind. Eng. Chem.*, 1935, **27**, 416. (Production of butyl and isopropyl alcohols by fermentation.)
 S. C. PRESCOTT and C. G. DUNN, *Industrial Microbiology*, McGraw Hill, New York, 1946. (Theoretical and practical aspects of all types of fermentation processes.)
 J. RAMSBOTTOM, *Brit. Assoc. Adv. Sci., Annual Rept.*, 1936. (The uses of fungi.)
 M. STEPHENSON, *Bacterial Metabolism*, 2nd ed., Longmans, Green & Co., London, 1939. (Theoretical aspects of biochemical activities of bacteria.)
 A. C. THAYSEN and L. D. GALLOWAY, *Microbiology of Starch and Sugars*, Oxford University Press, London, 1930.
 C. THOM and K. B. RAPER, *Manual of the Aspergilli*, Williams & Wilkins Co., Baltimore, 1945. (Classification, morphology, physiology, useful and harmful activities of the genus *Aspergillus*.)
 A. WELLS and G. E. WARD, *Ind. Eng. Chem.*, 1939, **31**, 172. (Discussion of fermentation processes.)
 WILSON, *Chemistry of Leather Manufacture*, 2nd ed., 2 vols., Reinhold Publishing Corp., New York, 1939.
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CHAPTER 6

DEXTRIN AND BRITISH GUMS

DEXTRIN, as understood commercially, consists of the degradation products obtained by treating starch in a variety of ways. It is liable to contain soluble starch and sugar, according to its degree of conversion, some dextrans approaching soluble starch in their composition, others being not far removed from glucose. Dextrin appears on the market in several forms: as powders varying in colour from white, through yellow, to brown; as granulated particles resembling gum senegal in appearance; as thick, viscous, coloured liquids or as a white paste. All of these contain a mixture of true dextrans.

In 1811 Kirchhoff¹⁵ obtained a gummy substance by heating starch in the presence of an acid, but the production of dextrin by roasting starch appears to be due to B. Lagrange, who published his method in the same year that Kirchhoff reported his work on the production of starch sugar and dextrin by the action of acid on starch. Later, the treatment of starch with sulphuric acid was further investigated by Biot and Persoz,¹⁶ who examined the products obtained and gave to the gummy material they separated the name 'dextrin,' because of the direction of its optical rotation. The product known to the trade as 'British gum' had been discovered previously, according to authentic sources, owing to a fire breaking out in a Dublin textile mill in which starch was stored. The brown-coloured powder which was left after the fire had played on the sacks was found to be soluble in water and to give a sticky solution. It was then discovered that the same result could be obtained by heating the starch in an iron pan.

Scientifically classified, dextrans are the degradation products of starch having the same empirical formulæ as the original starch, i.e. $(C_6H_{10}O_5)_n$. In starch the value of n is fairly large, but in dextrans it progressively decreases as the degradation of the starch continues. The pure dextrans are soluble in water, insoluble in alcohol, and with iodine solution give either a blue, violet, red or a brown coloration, or no colour at all.

The physical properties of dextrans vary greatly with the method of treatment.¹ Some, when dissolved in water, give thick,

viscous pastes. others thin flowing liquids ; some dry quickly when exposed to the air, whilst with others the process takes place slowly ; with some the viscosity of their solutions does not alter appreciably on storage, whereas solutions of others show a decided increase in viscosity with age, and also the phenomena of ' retro-gradation ' or reversion, becoming cloudy or pasty according to the degree of reversion. Generally, the further the conversion is carried the more stable is the resulting dextrin and the less it tends to show reversion, although this applies less to mixtures containing caustic soda and borax.

It will be readily seen that there is no absolute method for referring to an industrial dextrin. Users are accustomed to order the dextrin they require according to the trade- or code-number of their supplier, and if they wish to change their supplier, they have to submit a sample of the required dextrin to the proposed new supplier for matching purposes. A more definite classification has long been wanted, and the author has found that if the starch from which the dextrin is made is specified, as well as the viscosity at 50° C. of a 1-1 solution of the dextrin in water, a better and more exact description is obtained. Thus, a yellow potato dextrin of good solubility, sugar-content of 2.5 per cent., moisture-content of 11 per cent., which yields a fairly adhesive solution, would, under this classification, be termed yellow potato dextrin, 57. The dextrin is dissolved in the water at 80° C., making allowance for its moisture-content, and the solution allowed to cool at 50° C., when its viscosity at that temperature is determined. This method was found to work quite well in one factory,¹ but is by no means claimed to be the best that could be evolved, and is open to some objections.

It is sometimes said that the process of making dextrin is highly complicated, and that secret processes are the rule, but such statements are quite unfounded. The process is well known and simple, being more of a craft than an exact science, and experience is required to get the best results. It is this fact, together with the general lack of enthusiasm on the part of makers to give any indication of how they obtain their products, which has probably given rise to the secret-process myth.

Methods of Manufacture.—In the manufacture of dextrin the processes used fall naturally under two main headings, the Torrifaction or Dry Method, and the Wet Method. In processes embraced by the first title the starch is heated, either alone or in the presence of small amounts of a catalyst, generally an inorganic acid ; in the second, the starch is suspended in water and heated with a catalyst or, after forming a paste, it is treated

with enzymes. The wet method of making dextrans will be dealt with later.

J. R. Katz³⁴ considers that dextrans and British gums made by heating dry starch at about 180° C. are closely analogous to those obtained by boiling starch with dilute acids or treating it with amylolytic enzymes, but, as we shall see, their properties may differ widely.

If starch is heated to a relatively high temperature, say about 160-190° C., it gives up its moisture, turns first a yellow and then a brown colour, and is then found to be soluble in water. The product known as 'British gum' has a strong smell, poor flavour, and gives deeply coloured solutions. The addition of a little nitric or hydrochloric acid to the starch before heating allows these reactions to take place at a lower temperature, so that the flavour, odour and colour of the product are markedly improved. Bloede¹⁴ appears to have been the first worker to exploit the acid-roasting process on a commercial scale in America, and in his original patent the starch was sprinkled with nitro-hydrochloric acid and then heated on iron plates in an oven.

In the method involving the use of an acid, the first product formed is soluble starch, and after this three stages, merging into one another, may be distinguished, viz. the formation of amylo-dextrin, erythrodextrin, and achroodextrin, in that order. By continued action of the acid on the last substance dextrose is produced, and by further heating at a high temperature the sugar appears to revert partly to dextrin, but this point has not yet been fully cleared up.

The various stages described above are readily recognised by the colours which their solutions give with a few drops of iodine solution, and this test is one of those used in factory control. When treated with iodine solution, a solution of the soluble starch first formed gives a blue coloration, a preponderance of amylo-dextrin gives a violet, erythrodextrin a red-brown coloration, and achroodextrin a pale brown or colourless solution.

Raw Materials.—Starch is generally used for making dextrin, but dried and ground tubers of potato or cassava plants may be employed, in which case a higher temperature, more catalyst, and a longer period of heating are needed in order to obtain the same degree of conversion as with starch; and an additional process of solution in water and filtration is necessary to obtain a usable product.

Maize, potato, and tapioca starches are most used for dextrin-making, and although rice and wheat starches can be used, they offer greater difficulties to conversion without any particular gain

in the way of special properties. The starch should be of the finest quality if a good lustrous dextrin is required, especially if the product is to be used in paper-making, where black specks or discoloration would condemn it at once. The choice of starch depends on the type of product required and the market price of both commodities.

Maize dextrin has quite a distinctive odour and flavour, but for cheap work it is extensively used, especially in the United States. For high-class work potato and tapioca dextrins are well established, and the latter is especially valuable, as it has a slightly greater strength than potato dextrin and at the same time is relatively odourless and tasteless, so that it can be used in adhesives for postage stamps, envelope-flaps, labels, etc., where the bitter taste of potato dextrin would be a disadvantage. Maize dextrins, made by the roasting process, are often used in conjunction with inorganic salts (see Adhesives) for adhesives without the addition of any other type of dextrin; maize dextrins made by enzyme-conversion are used as the basis of certain adhesives to which are added potato or tapioca dextrins to impart desirable adhesive properties; such a composition forms the basis of some of the best photographic mounting pastes on the market (see p. 123).

The mode of preparation of the starch during manufacture sometimes affects the ease of conversion, and it has been asserted that starch free from any traces of sulphur compounds is less liable to give rise to fire hazards than starch containing them. This may or may not be true, but in regard to fire hazards, it should be mentioned that the provision of ample window space in the factory is one of the best methods of minimising damage should an explosion take place.

The rate of conversion to dextrin of a particular starch can be judged with some accuracy from its average grain size—the larger the granules the more readily is the batch converted to dextrin. The starches with the smaller granules, such as tapioca or maize starch, require a higher temperature than potato starch, and this rule appears to hold for individual deliveries of starch. It has been stated that the presence of small amounts of hydrocyanic acid slows down the conversion, especially that of tapioca starch, but as other starches which are known to contain no hydrocyanic acid show variations in ease of conversion from delivery to delivery, this explanation does not seem tenable. The presence of alkali may explain the greater usage of the acid catalyst required in some cases, but this does not explain why some starches cannot be fully converted even in the presence of great excess over that

normally used of the hydrolytic agent. It is significant, however, that the lower-grade starches show this effect much more frequently than the high-grade starches, but a good-grade starch which has been separated by a centrifuge method is likely to contain all the small granules present in the liquor and to show this resistance to conversion into dextrin to a small degree. We have not seen this explanation put forward before and, if the difficulty of gelatinising the smallest starch granules with water is taken into consideration, it appears to fit most of the facts. Another interesting point which probably has some bearing on the above observation is, that batches of starch having a smaller average particle size than usual are more liable to give the unstable type of dextrin which, although its solutions have the correct viscosity when first made, show an increased viscosity on standing and also the phenomenon of retrogradation to a marked degree. Such dextrans will give perfectly clear solutions when dissolved in water, but these solutions on standing for 24-48 hours appear quite pasty or opaque. To overcome this drawback, the time of maturing, the amount of acid catalyst used, or the conditions of roasting employed to produce the type of dextrin required from a normal starch, may have to be adjusted so as to obtain the desired product. As alteration in any of these values is liable to give rise to corresponding changes in the amount of sugar formed, the statement that dextrin manufacture is an art and not a science will be appreciated.

Starch containing sulphites gives a paste which has a lower viscosity than that which has been freed from these compounds, and the first stages of the conversion of such a starch may proceed rapidly.

The Choice of Acid.—As already stated, hydrochloric and nitric acids are both suitable for use in dextrin-making, but sulphuric, nitro-hydrochloric, oxalic and phosphoric acids have all been employed, and especially the first two of these. For use in the conversion process, an acid should not leave any residue on evaporation, which in the presence of iron salts is detrimental to the final colour of the dextrin. There is, however, a patent² in which certain metallic chlorides and nitrates are added to the acid to check its evaporation during the roasting process, thus shortening the time required. It is claimed that this addition decreases the acid consumption, and that a practically pure white product of very good solubility is readily obtained. In one example in this patent, 100 kg. potato starch are heated for 40 minutes at 120-130° C. with 5 litres of water in which 150 ml. concentrated hydrochloric acid and 20 grams manganous chloride

are dissolved. A. E. Williams³ states that he has tried this process, but that no marked advantage could be obtained. A slight shortening of the time of conversion was noted, but it would appear that the process is of no special interest, especially as such dextrans cannot be used in food manufacture.

As previously mentioned ground tubers have been used to prepare dextrinised products. W. S. Bowen³⁹ produces dextrin from partly gelatinised potatoes by mixing with a slightly acid mixture of salts and drying. He claims, as a suitable salt mixture, that consisting of 8 per cent. ammonium chloride, 20 per cent. sodium chloride, 62 per cent. calcium dihydrogen phosphate and 10 per cent. calcium phosphate. Such dextrinised products have very limited or specialised uses and the above product is claimed as a flour improver and yeast activator. The writer has successfully converted dried, ground cassava tubers in their entirety for use as a low grade adhesive. The heating and acid required, however, were excessive.

As will be seen later, an indication of the acid used in its manufacture is given by the colour of the dextrin to be matched. The conditions of roasting have to be carefully watched when sulphuric or phosphoric acid is used, but the volatile acids allow some little latitude, and should be given preference as during the heating process they vaporise and penetrate the mass of starch, giving a more uniform distribution of catalyst throughout the mass. Phosphoric and sulphuric acids give products which are inclined to be more than usually hygroscopic. A further point in favour of the volatile acids is that they evaporate during the roasting, and hence the end-point of the roasting can be more readily controlled. The treatment of starch by means of the hot vapours of acids, such as hydrochloric or nitric acid, is sometimes used on a commercial scale. Spraying the hot dextrin with 3-5 per cent. formaldehyde after the acid treatment is finished gives a product which is more soluble but unaffected with regard to viscosity and colour.

The hygroscopicity of a dextrin and a tendency for its solution to be stable or otherwise depend largely on the presence of dextrose, and the amount of dextrose formed during conversion is largely dependent on the acid used and on the time and the temperature of processing. O. Philipp¹⁷ appears to have been the first worker to note that the amount of acid influences the amount of sugar formed in a conversion. The volatile acids give lower values, generally speaking, than the non-volatile acids in this respect. S. P. Aiger³⁵ mentions that rice starch requires five to six times the amount of acid for conversion as does potato starch.

Pre-treatment of Starch before Torrification.—Various processes have been patented and are in use by which the starch is treated in some way before the actual roasting process is carried out. The National Adhesives Co.⁴ sensitises the starch to the action of acids by treating with hypochlorite solutions, adjusted to the *pH* value necessary to give any desired characteristic to the finished product. This process also destroys certain impurities that may be present in the starch and allows of the preparation of finer coloured products than would otherwise be possible. The treated starch appears to contain some combined chlorine, and the presence of calcium chloride acts as a catalyst in the subsequent conversion to dextrin. In certain cases, where a particular type of glue containing calcium chloride is to be made, the presence of this salt due to the pretreatment is immaterial. The catalyst may also be incorporated in the magma of starch after the chlorination is complete, thus giving a more uniform distribution. The drying and dextrin-formation in this instance may be effected at the same time. In Böhme's patent⁵ the main bulk of the starch is swollen before it is mixed with a small amount of powdered starch containing all the catalyst necessary to convert the whole mass to dextrin, and then heated to 105–150° C.

Another process that has considerable vogue is the drying of the acidified starch before torrification; this will be discussed later.

Main Steps in Dextrin Manufacture.⁶—The following are the main operations carried out in dextrin manufacture. It will be seen that some of the steps may be omitted, according to the design of the plant or the preference of the operator :—

1. Addition of the catalyst.
2. Maturing (optional).
3. Drying (optional).
4. Roasting or torrification.
5. Cooling.
6. Re-moistening.
7. Grinding and bagging operations.

In some processes the starch is acidified and then roasted immediately, in others the starch is actually acidified in the roasters.

Addition of Catalyst.—A small batch of starch may be mixed with the requisite amount of acid, and this acidified powder is incorporated with the rest of the starch.⁵ A much more satisfactory method, however, is to spray the acid, by means of an atomiser-jet,^{18–21} on to the starch, which is suitably agitated

during the addition. Air under pressure—about 20 lb. per square in. suffices—is used to force the acid through the fine jet so that it meets the starch in the form of a very fine mist. The acid is generally first diluted with two to five times its volume of water, and additional catalysts such as inorganic salts may be added to the solution or sprayed on separately, according to their compatibility with the acid.

The amount of acid used is generally smaller for potato starch than for maize or tapioca starches. To obtain a white potato dextrin, about 80 ml. of hydrochloric or nitric acid can be diluted to 300 ml. with water and sprayed onto 100 kg. starch. This amount may have to be increased or decreased according to the particular delivery of starch. For a tapioca dextrin, 200 ml. of either of the above acids is diluted to four times its volume with water and added to the starch; this figure, again, is only an approximation. Some tapioca starches give a pink shade when nitric acid is added, but others remain white. This affects the final shade of dextrin, and the cause of this colour change has, so far, remained unexplained.

When hydrochloric acid is used as the catalyst it may be added in the form of the gas in a machine similar to the remoistener (v.s.). Air dry starch containing approximately 12-20 per cent. water, readily absorbs the gas but the acid does not penetrate the mass of the starch. Both the absorptive capacity and the resistance to penetration of the acid decreases with decrease in the water content of the starch so that when a water content of 3-4 per cent. is reached sufficient hydrochloric acid gas is absorbed and penetration is sufficient to enable dextrinisation to be readily carried out when roasted at 180-193° C.³⁸

A patent⁴⁰ has been issued for this method of using a water-soluble gas giving a mineral acid with the water of the starch.

Maturing the Starch.—By the term 'maturing' is meant storing the starch so as to allow the catalyst to diffuse thoroughly throughout the mass, and the slow conversion of the treated starch into the soluble modification. When the starch is ready for processing it will rapidly dissolve in water at 80° C., and the longer the maturing, the more quickly will the formation of dextrin take place and the lower will be the temperature required for the conversion. The maturing may take anything from 12 hours up to 5 days to reach the required stage, the starch generally being stored in hardwood bins during this time. A well-matured starch gives a better coloured dextrin, and shows better stability for the same degree of conversion than one which has been inadequately matured. When ready for processing, the starch is

withdrawn from the bottom of the bin by a conveyor. This process is by no means always used, but is employed in a number of factories on the Continent and by a few in England.

Drying the Starch before Roasting.—This step is quite optional, and many factories omit it entirely. Bloede,²⁵ by heating and pre-drying starches before roasting, obtained them in a very dry state, and from such dried starches he obtained dextrans that differed from those obtained by roasting the same starches without this special pre-treatment. The moisture in the starch, including that added with the catalyst, is often expelled in the roasters by careful adjustment of the temperature. In the process in which the starch is matured, however, removal of the moisture before the starch reaches the roasters constitutes an important step. If the starch is insufficiently dried, sugar is formed during the roasting in an amount depending on the percentage of residual water. Owing to the rapid conversion which takes place in the roaster, the temperature and time of roasting cannot exceed certain limits, so that the re-conversion of sugar to lower dextrans cannot take place. In the generally used older processes, however, a longer time of roasting is required, viz. some 3 hours, together with a somewhat higher temperature, and thus some of the sugar formed initially appears to be reconverted into dextrin or dextrin-like substances.

Drying may be carried out in the roaster by cautious heating and agitation, or in a vacuum dryer. In the latter method, care must be taken that the temperature of the jacket is not raised too quickly, as when this happens the starch forms lumps coated with a gelatinised starch, thus preventing thorough expulsion of the water. Potato starch seems more liable to this defect than other starches, probably owing to the greater amount of water present in the first instance, and partly to the greater ease with which it gelatinises. It is a good plan to start the vacuum pump about 5 to 10 minutes before the steam is admitted to the outer jacket. The degree of vacuum is generally about 25-26 inches. The temperature in the vacuum chamber is allowed to rise to about 70° C. in about 30 minutes, and then the starch is generally ready to discharge. Some batches of starch are much more easily dried than others, and are ready in 10 to 15 minutes, but the reason for this is unknown to the author. The progress of drying can be watched by means of a gauge in the water-trap fitted to the drier. Some starch coming over as dust also collects in the water-trap; it is removed with the water at the end of each run and collected by sedimentation.

A certain amount of acid, especially when a volatile acid is

used as catalyst, is found in this water, and amounts to approximately two-thirds of the quantity of acid added to the starch in the first place. The starch from the dryer is often half-way to the stage of conversion to which it is to be taken, depending on the batch of starch; the content of reducing sugar varies from 1.5 to 3.5 per cent., or even higher, and the moisture-content is about 3 per cent. when it is passed to the roasters.

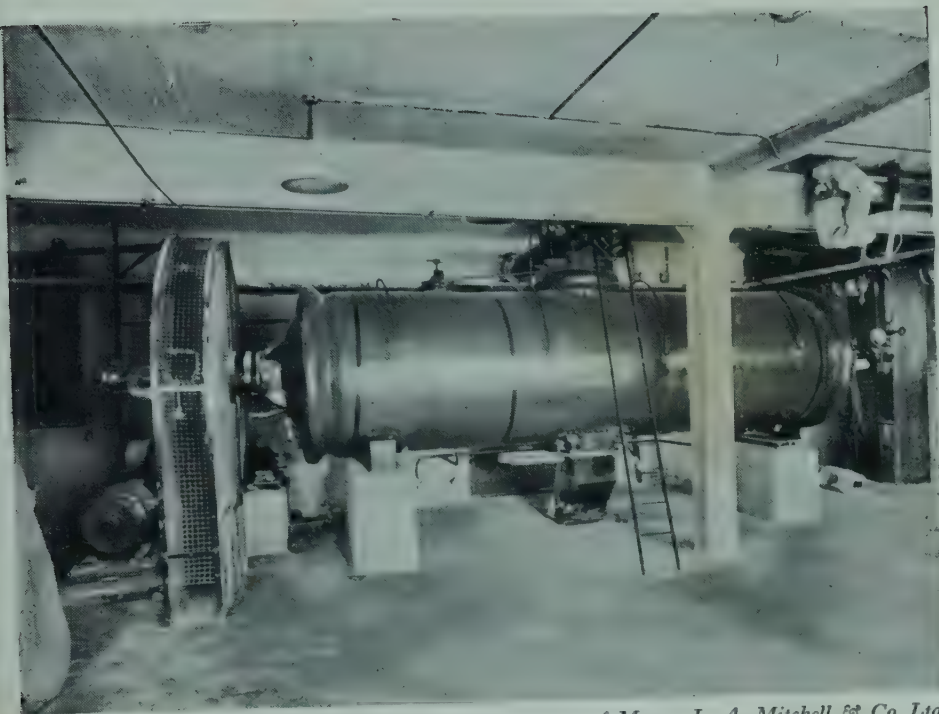
The Roasting Process.—At one time the starch was moistened with the catalyst solution, shaped into bricks, and heated on trays in a heating-room at about 95-150° C. Now, heated pans or vessels are used that are fitted with an efficient stirring device, for one of the main essentials of the process is that the starch should be uniformly heated: at no point should the starch be stationary or the temperature exceed that of the rest of the vessel.

Many factories employ steam-jacketed pans in which to roast the starch, the jackets withstanding a pressure of 100 lb. steam, which gives a temperature sufficiently high for the production of most, if not all, dextrins, but not for British gums. The highest temperature required for a dextrin is about 180° C., whereas for British gums over 200° C. is necessary. Tapioca dextrin requires the higher temperature-range of 140-175° C., whilst maize is often roasted in the region of 125-140° C., and potato starch is converted at temperatures between 105 and 135° C.

Uhland's apparatus contains heated oil in the outer jacket of the dextrinising vessel, and is very suitable for continuous working. Lehmann's dextrinising vessel is air-jacketed, the air-space below it being heated by conduction from a fire, or burners, along tubes containing water. The pressure within these tubes, which are sealed, is indicated by a manometer, and regulated to about 150 atmospheres. Many factories, however, still employ gas-fired roasters with every satisfaction.

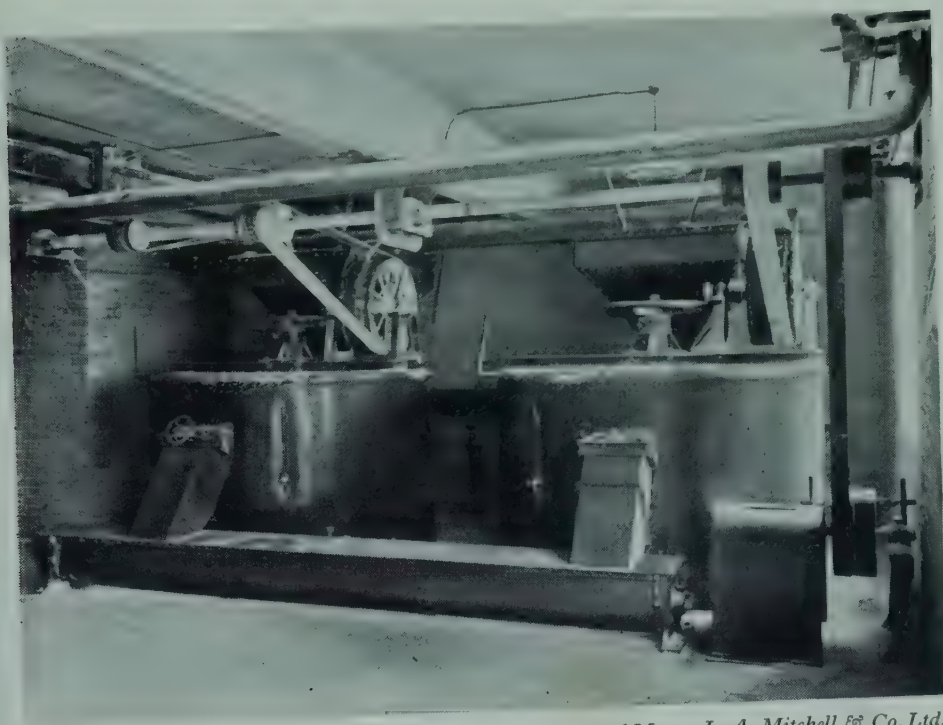
In one process, due to H. Wulkan,⁷ about 5 per cent. of the starch is mixed with the total amount of catalyst (0.2 to 0.4 per cent.) to be used, with little or no previous dilution, and then mixed with the remainder of the starch. This mixture is fed through rollers into a steam-jacketed vessel, where it is agitated and moved continuously towards the discharging device through which it is withdrawn as dextrin. As the operation is carried out in a more or less confined space, practically no moisture is lost.

Heating by steam appears to give most satisfaction from the points of view of ease of control and even distribution of heat, and superheated steam has sometimes been employed. In vessels using superheated steam an early trouble was experienced, in that the portion of the roaster near the inlet absorbed more of the heat



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FIG. 6:1. Rotary vacuum dryer of the batch type, for drying starch.



[Reproduced by courtesy of Messrs. L. A. Mitchell & Co. Ltd.]

FIG. 6:2. Hot-plate dryer consisting of mechanically agitated gas-heated pans for the production of dextrin. This type of dryer or roaster can also be arranged for steam or oil heating.

[Facing p. 116.]



[Reproduced by courtesy of Messrs. L. A. Mitchell & Co. Ltd.

FIG. 6.3. Continuous rotary cooler for dextrin.

than the rest of the vessel. Some roasters are now on the market in which this defect is largely overcome by having a number of inlets feeding into small compartments in the outside jacket. These small sections are each fitted with a water-condensate trap which automatically discharges any water formed.

Another type of roaster is heated by circulating hot oil in the outside jacket, and by this means temperatures high enough to obtain British gums can be obtained. Electrically-heated converters have been suggested, and should prove of value where electricity is cheap. The whole question of design of the roaster is purely one of engineering, in which a sufficiently high and yet evenly distributed temperature is the chief consideration to be kept in mind.

Some makers claim that under a partial vacuum the torrification process is speeded up, whilst others claim that the same object is achieved by roasting in closed vessels owing to the pressure set up by the liberated moisture. Krause⁸ considers that by removing the vapours from the surface of the material in the roaster the water is more rapidly eliminated and a better conversion is obtained, and he has designed a simple mechanism to this end. Roasting in an open vessel appears to be conducive to a lower sugar-content, owing to the moisture being able to pass away freely as it is given off. The author has not observed any speeding up of the process by the use of partial vacuum, but has found that the final sugar-content is lower than when the roasting is carried out at normal pressures.

By roasting under pressure, the conversion can be carried out at a lower temperature than at atmospheric pressure, and in the absence of a catalyst, but it is possible that some of the compounds liberated in the conversion of the starch to dextrin play a part. Under pressure dextrin forms rapidly, but the final product contains too high a proportion of sugar for some purposes, e.g. for the making of certain adhesives. Well-defined derivatives, the so-called achroodextrins, which are good adhesives, are obtained, according to Haake,⁹ by mixing 100 kg. potato starch with 0.2 per cent. hydrochloric acid, and exposing the mixture for 2 or 3 seconds to a pressure of about 2,500 kg./cm². without cooling. In this manner it is claimed that a very light-coloured product is obtained.

H. E. Bode³⁶ dries the starch under vacuum, and after treating with a water-immiscible liquid such as propylene dichloride in the absence of air, the starch is suspended in an oil and heated until converted to dextrin.

Generally speaking, the lower the acid-content of the 'mix'

the higher the temperature employed for roasting to obtain the same degree of conversion, and in making white dextrins care must be taken to see that the colour does not turn yellow, due to some starch grains being very easily degraded at the higher temperature required to convert the bulk of the mass. A high acid-content, inasmuch as it assists conversion, is generally conducive to a high sugar-content. As mentioned elsewhere, the content of sugar increases to a maximum, sometimes to as much as 10 per cent., and then falls to the final value found at the end of the conversion. The longer the time and the higher the temperature the lower the sugar-content, a result that seems due in part to reversion of the sugar to dextrins, or substances akin to them, and in part to the evaporation of the catalyst.

If a sample to be matched contains more than 2 per cent. sugar, it may be inferred that it has been made by an acid process; the amount of sugar in excess of this figure appears to run roughly parallel to the amount of acid used in the conversion.

In the manufacture of dextrin, when the temperature of the roaster has reached about $110-115^{\circ}\text{C}$. (or about 125°C . in the case of British gum) a small amount of retained moisture will come off as steam above the heated mass; but suddenly there will be an evolution of a cloud of steam, the temperature of the mass will rise by $5-10^{\circ}\text{C}$., and dextrinisation proceeds very rapidly. It would appear that some sort of anhydride formation with the elimination of water occurs at this point. No reference appears to have been made to this phenomenon in the literature of the subject although it must have been observed, as it is very marked.

When tests, to be described more fully below, show that the conversion has reached the desired stage, the hot dextrin is discharged into the cooling apparatus.

M. D. Rozenbroek³⁷ has covered a process in which air-dry starch is treated with a gaseous acid so that some 0.5 per cent. is absorbed on the starch, and after allowing the starch to lie in the acidified state for some 12 hours it is 'roasted' at temperatures below 80°C ., care being taken to maintain the moisture-content at that of the air-dry material.

Cooling and Re-moistening the Dextrin.—To prevent the conversion of the dextrin proceeding further than is desired, it is cooled immediately it is discharged from the roasters. Uhland's apparatus for this purpose consists of shallow, circular iron pans one above the other, each having a stirrer attached to a common shaft, which passes through the centre of all the pans. The dextrin is swept by each stirrer to the pan below, and the whole is cooled by a current of air.

In another apparatus (see Fig. 6:3) the dextrin falls into a long cylinder, slightly inclined to the horizontal, which is cooled by water passing through an outer jacket, and is moved by a stirrer towards the discharge door, through which it passes to storage bins to await re-moistening. Still another apparatus is a tower in which the falling, hot dextrin meets a countercurrent of cold, damp air.

Dextrin, after roasting, is a very hygroscopic powder. As sold, it contains from 8 to 14 per cent. of moisture, and the further it has been converted the less water will it contain. In some factories the moisture is put into the dextrin by spreading the powder on to trays and exposing it on a rack to the air. This method requires a lot of floor space. Another method is to use some sort of apparatus in which the fine powder falls from a height against a counter-current of moist air,¹³ or through a very fine mist produced by spraying water under about 5 lb. pressure through an atomiser-jet.

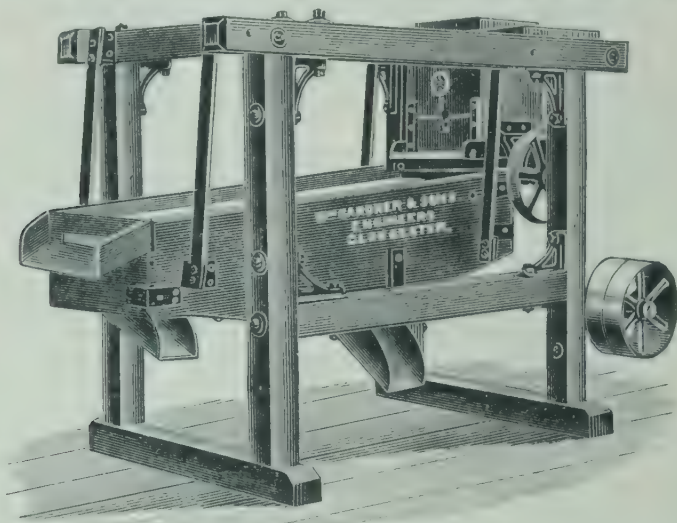
In one of these machines the dextrin can be re-moistened in 2-3 days, whereas by the tray method some 5-14 days may be required.

A further use for an apparatus of this type is that for spraying a chemical in aqueous solution which it may be desired to add to the dextrin. Potato dextrin, and other dextrans to a less extent, have an odour that is objectionable to some people. According to H. Kunz-Krause,¹⁰ this odour is due to a non-volatile cyclic ester of myristic acid, dextrinazol, which can be separated from the dextrin by a steam-distillation and can be obtained by the extraction of the distillate with petroleum ether. In this connection it is interesting to note that A. Payen¹¹ as long ago as 1846 obtained a yellowish oil by distillation of saccharified starch with dilute sulphuric acid which had an intense odour and to which he attributed the odour of starch.

To render this smell less apparent or to destroy it, Pieper¹² proposes to pass ozonised air through the roaster during the conversion. If a small amount of sodium sulphite or bisulphite, or hydrogen peroxide, is added to the water in the re-moistening apparatus the odour and colour of the resulting dextrin are very much improved. The sulphur compounds also act as preservatives for solutions of the dextrin, but unfortunately tend to impart a 'ropiness' to the gum so made. A further drawback to the use of reducing compounds for this purpose is that many dextrans are used in alkaline solutions, and the addition of alkali to the dextrin bleached in this manner restores its original colour. The use of oxidising agents for this purpose appears to be preferable,

as the colour is not restored to anything like the same extent as when it is bleached with reducing agents.

Grinding and Bagging-off Operations.—If re-moistened in one of the machines mentioned above, the dextrin invariably contains lumps resulting from the presence of excess water. It is



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FIG. 6:4.—A shaking sieve.



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FIG. 6:5.—Sifting and bolting machine.

therefore ground in a mill and passed through a rotary sieve (Fig. 6:5) covered with silk of the required mesh, any lumps and coarse particles being automatically returned to the mill for further grinding. A shaking sieve (Fig. 6:4) is sometimes used for this purpose. The powder falls into bins from which it may be transferred automatically to sacks. The dextrin thus obtained is

often blended with other batches in order to obtain uniformity of output or to obtain products which have special, desirable properties that are not readily attainable by adjustment of the catalyst or of the roasting conditions employed. The average yield of dextrin from 100 tons of starch is about 90 tons.

Conversion of Starch to Dextrin by the Wet Process.—

A very important process for the manufacture of dextrin is that involving the treatment of starch suspensions with acids or hydrolytic agents, the so-called wet process. The dextrins so obtained are always used, either for textile or for adhesive purposes. As previously mentioned, the sugar formed by the action of enzymes is maltose, whereas the action of acid to produce dextrins gives a certain amount of dextrose, which is more hygroscopic than maltose, and if present in excessive amounts causes cracking of the adhesive film with a consequent lowering of its strength.

Acid Conversion in the Wet Process.—Many tons of dextrin made by simply heating an aqueous starch suspension with an acid, such as hydrochloric or sulphuric acid, are made every month and marketed as adhesive pastes. Any of the hydrolytic agents used in the roasting process may be used, and when the hydrolysis has reached the required stage, as shown by viscometric measurements and the colour given with iodine, the action is stopped by cooling, and the acid present is neutralised. Some makers prefer to use acids which give white insoluble salts on neutralisation, such as sulphuric acid or phosphoric acid which have white insoluble calcium or barium salts, as in this way a good white paste is obtained at the end of the reaction.

The action can be carried out at various concentrations ; at the higher concentrations fairly viscous pastes are obtained which, after neutralisation, are strained and packed immediately. At lower concentrations, thin liquids are obtained which are evaporated to the required consistency after the action has been stopped. If the dextrins are to be used in coloured-paper work, it is preferable to use a lower concentration in order to obtain a completely neutral paste at the end of the reaction, the neutralisation being more readily controlled than with a thick paste. To obtain a product with superior odour, colour, and flavour, A. Schumann²⁶ treats starch with a 1 per cent. solution of an acid at room-temperature for about 24 hours, and after washing free from the acid, suspends it in water containing sulphurous acid ; he then heats the suspension under 40-50 lb. pressure until reducing sugar is detectable. The pressure is then released, the solution of dextrin passed through animal charcoal, evaporated to dryness, and ground. Another process,^{27, 28} employing heating under pressure,

is that in which equal weights of starch and water are mixed, acid to the extent of 0.5 per cent. on the weight of suspension added, and the mixture then heated under 20-30 lb. pressure. C. M. Higgins³³ obtained a solution of dextrin by suspending 5 parts of starch in 8 parts of water containing an acid catalyst, and maintaining the temperature at a point just below that at which the starch gelatinises; after a requisite period, he raises the temperature of the batch to above the gelatinising temperature, and finally neutralises the hydrolytic agent present.

This type of dextrin finds a ready outlet for many purposes in the stationery, paper-box making, and other trades dealing with paper goods in one form or another; it is useful for sticking the paper linings in cheap trunks and attaché cases and in certain textile dressings.

The Conversion using Enzymes.—The action of enzymes on starch has been discussed elsewhere (Vol. I), and in the adhesives industry wide use is made of the process for producing dextrins intended for special purposes. Sometimes the dextrins so obtained are used as pastes without any further treatment after the action has been arrested, but in other cases dextrins produced by the roasting process are added in order to increase both the adhesiveness and the total content of solids of the final paste. Maize starch gives very smooth pastes by this method, and is used by certain manufacturers as the basis of a photographic mounting paste.

Conversion with enzymes is conducted by treating the starch paste (obtained by heating starch with water) with malt extract, or with an extract or preparation containing some other hydrolytic enzyme. Malt diastase works best at pH 4.6, which may be allowed to rise to pH 5.2 without too great a detriment to the speed of the reaction. Takadiastase or similar enzyme may be used in place of malt extract and yields dextrins with good adhesive properties. Pancreatic diastase is most active when the pH value is around 6.9, and the activity of pancreatic amylase is increased by the addition of common salt.

In carrying out a conversion, the conversion-vat should be thoroughly cleaned before charging and copper or brass fittings should not be used, because traces of copper salts inactivate diastase. The temperature of conversion should be 65-70° C., in order to reduce the formation of sugar during the reaction. The production by this method of a product consisting chiefly of amylopectin and maltose is described later (*v.i.*). The reaction is generally stopped when it has reached the required stage by heating for a short time to a high temperature to de-activate the

enzyme, and by neutralising the batch so that the conditions are unfavourable for enzyme action. Occasionally some batches of starch are rather more difficult to convert than others, and this resistance appears to be due to an inherent property of the starch itself, and not to outside factors, as the resistance of a particular starch appears to depend largely upon the conditions and time of cultivation; but this difficulty is not often experienced in the ordinary course of factory processing.

Nitze²⁹ has attempted to shorten the process of obtaining dried dextrans by enzyme action by mixing potato starch with an equal weight of water and 1 per cent. its weight of malt diastase, and passing the mixture over hot rollers so that the starch is gelatinised, hydrolysed, and dried in quick succession. In a similar process, Buhtz³⁰ uses compressed yeast for conversion instead of diastase.

Stern³¹ carries out the conversion, using diastase at a temperature of 70° C., which is just below the killing-point of the enzyme, and in this way the sugar-forming element present is retarded in its action, as previously mentioned. Stern treats a suspension of 30 kg. potato starch in 40 kg. water with about 5 litres of malt extract for 15 to 30 minutes at about 70° C., and dries the mass *in vacuo*. In this manner a mass containing 70 per cent. dextrin is obtained which can be further treated, according to another patent by Stern,³² with yeast, which ferments the sugar present without affecting the dextrin, thus freeing the mass from sugar.

A good maize conversion¹ suitable for making an adhesive paste for use in photographic mounting, may be made as follows: The tank is cleaned and 1,000 lb. water run in, and the pH value adjusted by the addition of sulphuric or hydrofluoric acid to 4.6, using bromcresolgreen as the indicator, after which is added 1,000 lb. of maize starch, the suspension being stirred from 15 to 30 minutes, or during the time the temperature is being raised to 55° C. At the end of this time, the pH value is again adjusted to 4.6, using acetic acid, 20 lb. of malt extract is mixed with 50 lb. of water and 28 lb. of this solution added to the tank, the temperature raised to 65° C. and maintained thereat for 15 minutes, the contents of the tank being efficiently agitated during the whole of the processing. At the end of these 15 minutes, another 7 lb. of the malt solution is added and the temperature raised to 69° C. for 15 minutes, then to 73° C., at which point it is maintained for 2 hours. Finally, the batch is heated to 95° C. and cooled to 73° C., when a test portion is withdrawn, and if the viscosity is not correct, another 7 lb. of malt extract solution is added and the conversion allowed to proceed until the required viscosity is

attained. About 5 lb. of caustic soda solution (70° Tw.) is then added to neutralise the acid present.

The above conversion is mixed with yellow potato dextrins for the production of strong quick-drying adhesives for paper cartons. For cardboard tubes, or for a craddy tray gum, a potato starch may be used for making the dextrin. The amount of sugar present in such conversions is about 7-8 per cent. After the starch has been converted into dextrin by the action of enzymes, the mass may be dried by passing it round hot rollers.

REFERENCES

1. J. A. RADLEY, *Chem. Trade J.*, 1936, **98**, 21.
2. PERL and STEINITZER, G.P. 456,841.
3. A. E. WILLIAMS, *Ind. Chem.*, 1933, **9**, 52.
4. NATIONAL ADHESIVES Co., E.P. 383,778.
5. BÖHME, G.P. 252,827, 286,362.
6. J. A. RADLEY, *Manuf. Chem.*, 1936, **7**, 5.
7. H. WULKAN, E.P. 7032, 1910; U.S.P. 993,011, 1911; Austr. P. 44,009.
8. KRAUSE, G.P. 549,711.
9. HAAKE, G.P. 573,420.
10. H. KUNZ-KRAUSE, *Ber. Deut. Pharm. Ges.*, 1923, **33**, 149.
11. A. PAYEN, *Compt. rend.*, 1846, **23**, 487.
12. PIEPER, E.P. 9675, 1894.
13. UHLAND, E.P. 363,623, 1906.
14. V. G. BLOEDE, U.S.P. 61,991, 1867.
15. G. S. C. KIRCHHOFF, *Mémoires Acad. Imp. Sci. Petersburg*, 1811, **4**, 27.
16. BIOT and J. PERSOZ, *Ann. Chim. Phys.*, 1833, **52**, 72.
17. O. PHILIPP, *Zeit. Chem.*, 1867, **10**, 400.
18. BLUMENTHAL, G.P. 11,120, 1880.
19. FIELDING, E.P. 20,488, 1906.
20. CALICO PRINTERS' ASSOC., E.P. 19,499, 1903.
21. BROWNING and BARLOW, U.S.P. 773,469, 1904.
22. E.P. 16,362, 1914.
23. U.S.P. 1,159,591, 1,159,592, 1915.
24. E.P. 336,903, 1903.
25. V. G. BLOEDE, U.S.P. 1,324,332, 1919.
26. A. SCHUMANN, E.P. 5460, 1887.
27. W. McLAURIN, U.S.P. 1,283,839, 1915.
28. — U.S.P. 1,284,120, 1916.
29. H. NITZE, G.P. 407,789, 1920.
30. BUHTZ, G.P. 544,879.
31. STERN, G.P. 523,349.
32. — G.P. 409,499.
33. C. M. HIGGINS, E.P. 1885, 1900.
34. J. KATZ, *Rec. Trav. chim.*, 1934, **53**, 555.
35. S. P. AIGER, *Bull. Dept. Agric. Burma*, 1937, **33**, 5.
36. H. E. BODE, U.S.P. 2,156,488.
37. M. D. ROZENBROEK, B.P. 544,245, 27/12/39. (Appl. 27/12 1938.)
38. L. T. SMITH and S. G. MORRIS, *Ind. Eng. Chem.*, 1944, **36**, 1052.
39. W. S. BOWEN, U.S.P. 2,185,368.
40. SOC. OF AGRICULTURE, U.S.P. 2,359,378, 1944.

ADDITIONAL REFERENCES

- F. LIPPMANN, *Zeit. Spiritusind.*, 1902, **25**, 237, 249, 269, 291, 304, 316. (Manufacture and testing of dextrins.)

- H. F. BAUER, *Eighth Int. Cong. Appl. Chem.*, 1912, **13**, 9. (Effect of acidity and time on the roasting of dextrins.)
- E. PAROW, *Zeit. Spiritusind.*, 1912, **35**, 507, 519. (Roasting processes for dextrin-making discussed.)
- M. FREIBERGER, *Farben-Ztg.*, 1913, **24**, 293. (Wet processes for dextrin manufacture discussed.)
- F. C. FRARY and A. C. DENNIS, *J. Ind. Eng. Chem.*, 1915, **7**, 214. (Dextrin-making using HCl.)
- S. E. WARDELL, *Amer. Gas Eng. J.*, 1917, **107**, 561. (Suggests gas is best means of heating roasters.)
- J. MORNINGSTAR, *Col. Trade J.*, 1918, **2**, 67. (General.)
- M. YANO, *J. Chem. Ind. Tokyo*, 1918, **21**, 865. (Dextrin from sweet-potato starch roasted with nitric acid.)
- W. A. DARRAH, *Chem. Met. Eng.*, 1924, **30**, 825. (Equipment and difficulties discussed.) U.S.P. 1,524,340, 1925. (Dextrin roasters heated by hot gases.)
- J. A. RADLEY, *Chemical Ind.*, 1936, **38**, 257. (Manufacture of dextrin by wet and by roasting processes described.)
- INT. PAT. DEVEL. CO., E.P. 453,132, 1936. (Vegetable proteins added to dextrin.)
- ANON, *Gel. Leim Klebst.*, 1934, 237. (Dextrin by acid process.)
- A. E. WILLIAMS, *Chem. Trade J.*, 1934, **95**, 273. (Oil process.)
- *ibid.*, 1936, **97**, 447. (General.)
- H. PRINGSHEIM, G.P. 279,256, 1913. (Use of *B. macerans* claimed.)
- K. MIYAJI, *J. Agric. Chem. Soc. Japan*, 1936, **12**, 851. (Dextrin produced as by-product of mannitol fermentation.)
- K. MYRBÄCK, *Svensk. Kem. Tid.*, 1937, **49**, 145. (Molecular weight.)
- STEIN HALL MFG. CO., U.S.P. 1,938,574, 1933. (Dextrin from grain.)
- HÖPPLER, *Gel. Leim Klebst.*, **7**, 75. (Concentrating dextrin solutions.)
- K. FREUDENBERG, E. PLANKENHORN, H. KNAUBER, *Ann.*, 1947, **558**, 1-10; *Chem. and Ind.*, 1947, 731-5. (Describes preparation of Schardinger dextrins using *B-macerans*.)
- G. V. CAESAR, U.S.P. 2,131,724, 4/10/38; Appl., 26/8/36. (Tapioca flour heated alone to about 130° C., then 2-5 per cent. urea added and heating continued to obtain British gum type of product, having high viscosity in water.)
- J. E. CLEGG and F. C. HILLIARD, U.S.P. 2,127,205, 16/8/38; Appl., 7/5/36. (Maize or sago starch heated with 1 per cent. of 56 per cent. aqueous ammonia at 100° C. for 2 hours, then short period at 120° C., finally 4 hours at 180-200° C. to obtain dextrin.)
- CORN PRODUCTS REF. CO., U.S.P. 2,287,599. (Chlorine gas and mono chloro-acetic acid claimed as converting agent in the torrefaction process.)
- J. W. EVANS and W. R. FETZER, *Ind. Eng. Chem.*, 1943, **35**, 439. (Account of the precipitation of dextrins from corn syrup by methanol and the theoretical implications of their data in relation to the mechanism of starch conversion to glucose by acid.)
- J. L. BAKER, *J. Inst. Brewing*, 1941, **47**, 344. (Discusses the action of malt amylase on potato starch paste to give maltose, malto-dextrin and stable dextrin, the separation of these and their properties when isolated.)
- R. M. HIXON, *Rept. Agric. Res.*, 1940, Part II; *Iowa Corn Research Inst.*, 5th Ann. Rept., p. 65. (Solubility of glucose and maltose in various strength aqueous methyl and ethyl alcohols to determine best medium for separating the sugars from dextrin.)
- S. NEUMANN, B.P. 619,404, 6/12/46. (Dextrin humidified by introducing into air of controlled humidity circulated in a closed system, the per cent. R.H. being regulated by the admission of steam.)
- K. MYRBÄCK, *Svensk. Kem. Tidskr.*, 1946, **58**, 119. (Formation and constitution of limit dextrins from starch.)

CHAPTER 7

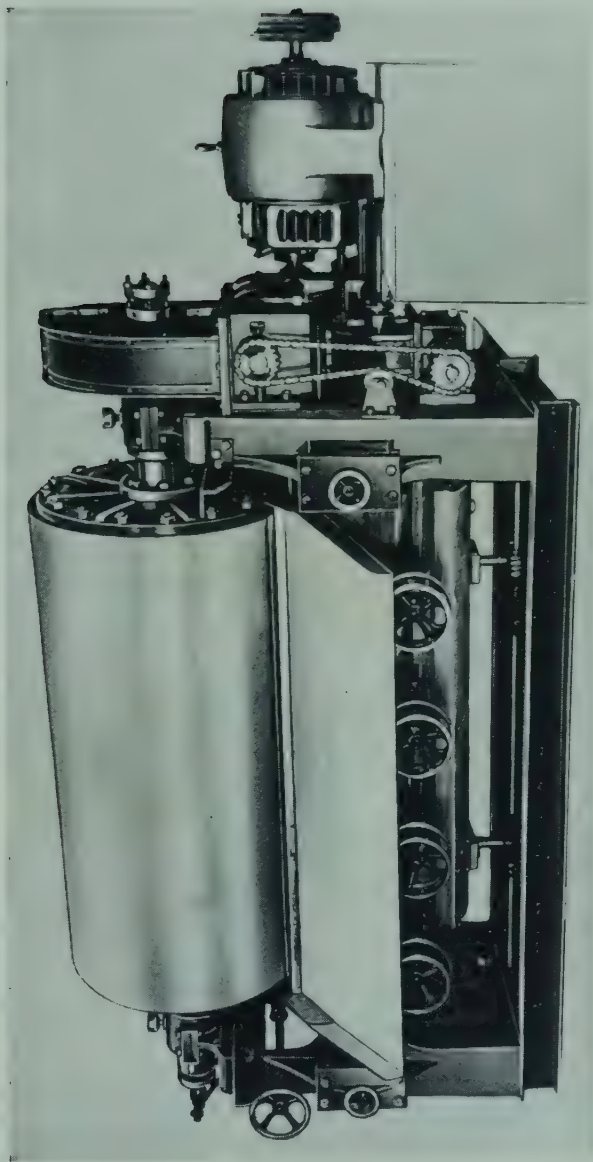
PHYSICALLY MODIFIED STARCHES

Physical Treatment to Modify Starch.—The effect of grinding a potato or a tapioca starch is to lower the viscosity of its solution, and it would appear that the longer the time of grinding, the greater is the fall in viscosity. The final point is reached when, on dissolving in water and allowing to stand, the solution forms two layers³ (see Vol. I).

G. Haake⁴ has made use of this property to obtain soluble starch by subjecting starch to the shearing action of rollers revolving in opposite direction and nearly in contact. The most favoured physical means of producing starch swelling in cold water is by the action of heat on moist starch or on the pastes. E. Wulkan⁵ heats starch to 110° C., and sprays water on it, so that small granules of paste are formed which dry almost at once. Schiedemantel⁶ spray-dries starch pastes in an inert or an active gas, as desired. Pfeiffer and Schwander⁷ heat starch above the paste-forming temperature and drop on to it water, which may contain chemicals for decomposing the starch. Small globules are formed and the process is very similar to one covered by Mahler and Supf.⁸ The latter workers obtain a cold-water swelling starch by taking the wet starch paste obtained in the manufacture of starch and passing it through heated rollers or drying it on drum-dryer (see Fig. 7:1).

R. W. G. Stutzke¹² modifies starch by forcing in under pressure in water through a heated tube and a spraying orifice into a drying atmosphere.

P. Petit and Richard⁹ have prepared an ordinary starch paste for mechanical conversion into a solution of soluble starch by passing the paste six times through an atomiser-jet under a pressure of 2½ lb., whereby a limpid solution is obtained. Milk of starch is atomised in a stream of hot air and steam in one patent,¹⁰ the starch becoming gelled. By using a modified spray-drier for this process a dry powder is obtained. A combination of some of the above effects has also been used,¹¹ the starch containing 25-50 per cent. of water being ground between hot rollers, which give a gelling, drying, and disintegrating action. Further instances of mechanical treatment to modify starch are given in



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FIG. 7:1. A drum dryer.

[Facing p. 126.]



the chapter on Adhesives. A rotary-beater machine is used by W. Seck,¹ both with² and without swelling agents, for preparing cold-swelling starches.

Most of the above methods give products that swell and form pastes with cold water, but they are not very different from the pastes made by heating the untreated starch with water, except those employing processes using excessive shearing or grinding action.

W. Seck and G. Fischer¹³ have studied the effect of extremely high shear velocities, such as can be obtained with a Hurrell colloid mill, on potato, arrowroot, cassava, corn, wheat, rice and sago starch pastes. Great reduction in viscosity is noted, in every case amounting in some instances to 98 per cent. These high losses can be correlated with the swelling properties of the various starches, those giving the highest degree of swelling without disintegration suffering the greatest reduction in viscosity. The viscosity differences between the untreated pastes disappear to a large extent when the starch is subjected to mechanical treatment, and this viscometric equalisation is probably due to the natural viscosity of the starch, uninfluenced by swelling or structural effects.

G. V. Caesar and T. D. Thompson¹⁴ obtain a starch product of unique homogeneity, stable viscosity and good film forming characteristics by repeatedly pumping a 5-30 per cent. solids raw-starch slurry under pressure through a restricted orifice. The frictional heat developed at the orifice is sufficient to gelatinise the starch. R. Sutra¹⁵ notes that ball-milling potato starch for 3 days gives a powder which immediately swells in cold water and the work of Lampitt, Goldenberg *et al.* on ball-milling wheat starch is discussed at length in Vol. I.

The chemical modification of starch to alter its properties is also dealt with fully in Vol. I and some further work on this subject is described under 'Adhesives' in the following chapter.

REFERENCES

1. W. SECK, E.P. 467,098, 1937.
2. — E.P., 464,606, 1937.
3. C. L. ALSBERG and E. E. PERRY, *J. Biol. Chem.*, 1925, **63**, 66.
4. G. HAAKE, E.P. 343,848. (Lapsed.)
5. E. WULKAN, U.S.P. 1,677,314.
6. H. J. BRAUN and H. SCHIEDEMANTEL, G.P. 401,361, 1922.
7. PFEIFFER and SCHWANDER, G.P. 445,557, 1924.
8. MAHLER and SUPF, G.P. 554,945. (See also G.P. 403,076, 1921.)
9. P. PETIT and RICHARD, *Compt. rend.*, 1926, **182**, 657.
10. METALLGESELLSCHAFT, A.G., E.P. 383,786. (Lapsed.)
11. INTERN. PAT. DEVEL. CO., E.P. 322,680. (Lapsed.)

12. R. W. G. STUTZKE, U.S.P. 1,516,512, 1924.
13. W. SECK and G. FISCHER, *Kolloid-Zeit.*, 1940, **90**, 51.
14. G. V. CAESAR and T. D. THOMPSON, U.S.P. 2,417,969, 25/4/1947.
15. R. SUTRA, *Bull. soc. chem.*, France, 1947, 738.

ADDITIONAL REFERENCES

- J. A. RADLEY, *Manuf. Chem.*, 1936, **7**, 246. (Soluble starches.)
- J. F. DEBUIGNE, F.P. 782,260, 1935. (Cold-swelling starch made in presence of gelatine, etc.)
- M. SAMEC and M. ZAKRAJŠEK, *Kolloidchem. Beih.*, 1937, **46**, 134. (Soluble starch from amylose.)
- G. LAQUEUILLE, *T.I.B.A.*, 1938, **16**, 677. (General.)
- W. B. NEWKIRK, *Ind. Eng. Chem.*, 1939, **31**, 153. (Industrial uses of soluble starches described.)
- SCHOLTEN'S CHEM. FABR., E.P. 494,927, 1938. (Moist starch and formaldehyde rapidly dried to give cold-swelling starch.)
- H. SCHORN and C. V. DAUMAS, U.S.P. 2,177,378. (Jets of superheated steam played on moist starch giving non-lumping cold swelling starch.)
- R. KISHORE and K. C. MUKHERJI, *J. Sci. Tech., India*, 1938, **4**, 27. (Preparation of starch and soluble starch.)
- W. A. NIVLING, U.S.P. 2,204,615. (Soluble starch prepared by carrying out reaction in gaseous medium.)
- CORN PRODUCTS REF. CO., E.P. 531,267, 11/7/1938. (Starch suspension pasted with steam and ground in current of hot air to give more modified product than 'Amijel' or 'Mogul'.)

PART II

THE INDUSTRIAL APPLICATIONS OF STARCH AND STARCH PRODUCTS

CHAPTER 8

ADHESIVES FROM STARCH AND DEXTRIN

THE field of adhesives is a very wide one, and to cover it completely from all points of view, including the theoretical and the manufacturer's, would be outside the scope of this volume ; hence attention will be directed solely to the adhesives made from starch and dextrin.

Starch adhesives were used by the ancient Egyptians whilst the use of flour for making papyrus was mentioned by Pliny¹¹² (see Vol. I) and ninth-century writing papers of Chinese origin were sized with starch. Decorative wall hangings appeared in France prior to 1630 and wallpapers stuck on with flour pastes were a natural development from these. Starch sizes and adhesives became much more common in the Industrial Revolution and in the U.S.A. John Biddis was granted a patent in 1802 for the manufacture of starch from potatoes.¹¹³ The introduction of postage stamps in 1840 and the subsequent invention of gummed envelopes gave a fillip to the demand for adhesives whilst, later, further impetus was given by the development of photography and the introduction of matches. The production of the tubular cartridge not only accelerated the development of the shotgun from the muzzle-loader but also laid the foundation of the cardboard tube industry. The paper bag and high-speed sealing by machines have developed into the vast packaging industry of to-day. Until 30 years ago animal glue was by far the most widely used industrial adhesive. It has been replaced by vegetable adhesives, nowadays, for many purposes and these also have special fields of use of their own. They are especially suitable for labelling and sealing by high speed, automatic machinery for manufacturing corrugated boxwood, plywood, envelopes, stamps and gummed tapes.

They possess the advantages of low price and can be applied cold or at moderately low temperatures, being reasonably lacking

in odour and taste. The latter point makes them especially useful in the food packaging industry or for any use where the adhesive makes contact with the tongue, e.g. envelopes and stamps, etc.

Purpose and Applicability.¹—One of the most important considerations affecting the manufacture of adhesives is the particular purpose for which they are intended. It might appear, for example, that if a starch paste affixes paper to glass firmly, it would serve in most trades which require to label bottles containing their products, but more mature consideration will show that it is not so.

Labels may be applied by hand or by machinery, and an adhesive which works well for the first purpose would not be suited to the latter, e.g. a tapioca starch paste (see p. 144) will work quite well for hand labelling, but on a machine, although it contains a lot of water, would not feed correctly, as it is too viscous and does not possess enough 'stick'. If it were to be thinned down to the required viscosity the large amount of water present would saturate the label and cause it to pucker on drying, and what 'stick' or tackiness the paste did possess previously would be seriously impaired.

A very tacky paste is not required in hand labelling, although in the machine it may be an important point, especially in a pick-up gum machine. Again, although the adhesive in this case must be tacky it must not at the same time 'fibre' or 'spin,' i.e. form long fine threads when two surfaces between which a portion of adhesive has been pressed are pulled apart. When an adhesive on a fast-working machine starts to spin, thousands of fine threads are very soon flying all over the place, which means that time is lost in stopping and cleaning the machine and replacing the poor batch of adhesive by a good one.

In this connection the following observation is of interest. A tapioca dextrin, fairly well converted, or a yellow potato dextrin, will give solutions in water which can be made to fibre, but if potato and tapioca starches are mixed in the correct proportions and together converted to dextrin, the product gives solutions which will not spin.

Sometimes the product has to resist water, as when used for affixing labels on champagne or wine bottles, and there does not appear to be any satisfactory starch adhesive to meet this demand, the addition of dimethylolurea to a starch glue might be of possible interest, as it has been patented for finishes on cloth to confer water-resistance. In other cases the addition of calcium or barium hydroxide confers some water-resisting power, but the effect is slight.

If a firm will accept returned empty bottles, the labels must be easily detachable when immersed in warm water or in the cleaning liquid of the washing machine ; straight starch pastes serve very well here.

So far we have only mentioned adhesives for use between a non-absorbing and polished body and one that absorbs some of the adhesive, but when we come to deal with rough surfaces, such as a wood-to-wood joint, different requirements are met. In a joint between two rough surfaces all interspaces must be filled with the adhesive, which must also firmly unite those portions that are in contact, the area of which is very much less than the surface area of the interspaces.

Thus the efficiency of an adhesive to bind together two rough surfaces will depend very largely on its viscosity ; it must be sufficiently fluid to penetrate the interspaces, and yet have enough body to give a thin but strong layer of adhesive when the joint is dry. With a comparatively rough surface the adhesive can 'key' itself into the material, and a rough parallelism between the strength of the joint and the strength of a thin film of the adhesive should exist as long as the adhesive is not stronger than the material it is joining. When other factors, such as rate of loading and relative humidity, elasticity, deformability, flexibility, stress and strain relations, are taken into account the determination of the tensile strength of a thin film of adhesive does give a good indication of its value in practice.²

F. Camps-Campins¹⁰⁶ has measured the pore size of a number of papers, and he points out that paper adhesives have to be formulated so that the penetrative properties have to counter-balance the pore size of the paper. Thus papers with small pore size require penetrative adhesives but those with large pores require a filming type of adhesive. Further, according to this worker, the pore size affects the rate at which the glue sets and also the behaviour of the wet glue films under pressure. The adhesive must be formulated, therefore, so that its properties compensate for these factors and for unequal porosities in the surfaces to be glued. Singleterry's¹¹⁴ observations are of interest in this respect as this worker has found that the adhesive is keyed to the paper by filling the undercut regions about the surface fibres giving mechanical keying.

The term 'deformability' is used to define the property of an adhesive to adapt itself readily to stresses and strains, slow or sharp, which may be set up in a joint after it has been made. While the adhesive is drying and setting, strains are set up in the joint by swelling, shrinking, warping, alteration either in humidity

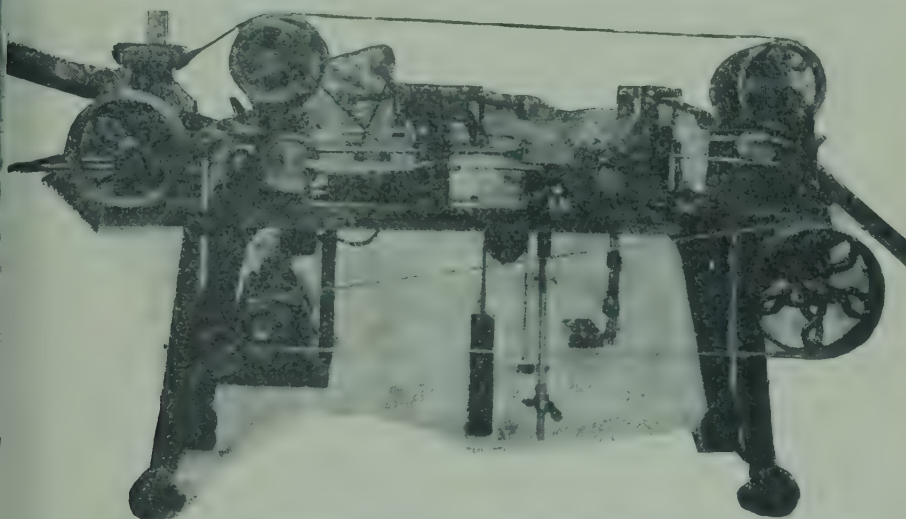
or temperature, and it is the deformability of a good adhesive which allows it to accommodate itself to new conditions as they occur and yet maintain a firm bond between the surfaces joined. In some adhesives the internal strains set up on drying are so great that the film flies to pieces ; an example of this kind is gum arabic or gum senegal. If, however, glycerine, glucose or some similar agent is added to the gum it acts as a plasticiser and confers deformability on the film, which then dries without disintegrating.

So important is this property that when measuring the tensile strength of an adhesive film it is quite as necessary to note its deformability as its strength, if the figures are to be of value in the practical evaluation of the substance as an adhesive. Colloids in general show this property to a greater extent than pure substances and are generally superior to them as adhesives. The following figures illustrate this point : Isinglass, tensile strength 13,000 lb. per sq. in., tough ; starch, 7,000 lb. per sq. in., ductile ; sodium silicate, 600 lb. per sq. in., very brittle ; gum-arabic, no value obtainable, very brittle. Gum-arabic splits up spontaneously on drying and dextrin pastes which crack on the surface should not be used to make adhesives for first-class work. If gum-arabic is plasticised, however, its strength immediately increases.

Rate of loading and humidity are important, and it has been found that long-continued stress on a joint, made between metals with recognised adhesives, reduces its ultimate strength. Another factor of interest is the thinness of the film of adhesive, as the joint-strength appears to increase with the thinness of the film over a wide range, providing the adhesive entirely fills the space between the two surfaces. A thick layer becomes less efficient as it ages, and this is especially important in tight wrappers, bottle-labelling, tin-labelling, and in sealing cartons. To obtain the best joint, therefore, the adhesive must entirely fill the space between the two surfaces and be present in a film as thin as possible. There appears to be some connection between the strength of certain joints and the mechanical properties of the materials being joined, such as tensile strength, elasticity and compressibility, but this relationship is at present obscure and little understood.

The Application of Adhesives.—There are about half a dozen different ways in which adhesives in general can be applied. Many can be applied by hand or brush, and others may be spread on to a sheet of metal, such as zinc, by a mechanical method and the paper, etc., pressed into contact and removed. The last method is the chief one used in many gumming machines, and in

order that the operation may be carried out at high speed much mechanical ingenuity and inventiveness have been shown in elaborating these machines. Most machines of this kind apply the gum by means of a roller (see Fig. 8:1), the thickness of the gum layer being determined by a doctor blade which scrapes excess glue off the revolving roller before it comes into contact with the material; in other machines brushes are used for the same purpose. When dealing with large surfaces spraying is very occasionally resorted to, but it introduces difficulties because viscosity and water-content must both be kept very low. The above methods are chiefly used with starch and dextrin adhesives.



[Reproduced by courtesy of the Beth Label and Wrapper Machines, Ltd.]

FIG. 8:1. The 'Beth' portable labelling machine.

For rubber, casein, or resinous adhesives, two other methods may be used; for example, two surfaces may be separately coated with the adhesive, which is allowed to dry and then pressed together with or without the application of heat. Alternately, a thin sheet of paper impregnated with the adhesive is placed between the two surfaces, which are then pressed together as above. This method is particularly suitable for resinous adhesives and a feature of the process is that no moisture is introduced.

The second method applicable to rubber and casein products is to make up two solutions and apply separately, or to mix just at the moment of application. Heat and pressure are often used to complete the reaction and form the joint.

The following hints in using adhesives are to be recommended; some of them may seem superfluous, but even so, in practice one finds that they are often ignored and lead to trouble:—

1. The surfaces to be joined should be as dry as possible,

e.g. in bottle-labelling the glass portion should be dry, otherwise blistering and wrinkling of the paper label may occur and the joint become unsatisfactory.

2. The surfaces should be as clean as possible and be especially free from oily substances. Although this suggestion may seem obvious, many instances could be quoted to show that it is necessary. Cosmetic and pharmaceutical products of an oily or greasy nature, which are being filled automatically into jars and bottles, are liable to be spilt. It needs only an extremely thin film of oil or grease on the bottle to bring about difficulties in the labelling machines.

3. Adhesives should be stored in a cool place, but not where they are liable to get frozen; this is especially important when the adhesive is a flour paste, as this type of product can be rendered absolutely useless by freezing.

4. If the air is unusually dry the containers of the glues can be covered with wet sacks, especially after they have been broached and some of the contents used.

5. Two different adhesives, bought in the ready-prepared state, should never be mixed, as each has been formulated with a fairly distinctive purpose in mind.

6. The adhesives used in machine work are preferably kept thick or 'heavy' in the glue-pots, but applied so that only a very thin film is transferred to form the joint. They should be tacky enough to produce a noticeable hissing on the machine when it is running, but should be so formulated that no 'webbing,' 'spinning' or 'fibring' takes place as the roller or glue-pad and the treated surface move apart. If the water-content of the adhesive requires some adjustment, the water should not be added to the glue-pot but the adjustment should be made prior to putting it in the machine, preferably by diluting it with a thinner mixture of the same adhesive.

7. Wherever possible, the two surfaces to be joined should be selected so that two hard surfaces do not come together, and at least one surface should be reasonably porous so that the adhesive can penetrate it and obtain a good 'keying' action. It is also advisable not to glue wrappers or labels too heavily to curved surfaces, owing to the strains set up within the film on drying.

Theoretical Considerations.²—When we come to consider adhesion from the theoretical aspect we are faced with several alternative theories. McBain and co-workers¹¹⁶⁻¹²³ distinguish between two kinds of adhesion, mechanical and specific. Mechanical adhesion takes place between rough surfaces, where the substance is permeable to the adhesive, by a keying action,

examples of such porous materials giving 'keyed' joints being paper and wood. Specific adhesion, or true adhesion is involved when smooth surfaces are joined since in these cases little or no keying action is possible. The main requirement for specific adhesion is the complete removal of adsorbed air or grease from the surfaces to be joined, i.e. the adhesive must 'wet' the surfaces. Under such conditions Van der Waal's force of molecular cohesion may be exerted. Specific adhesion is also dependent on the maintenance of contact between the solid and the adhesive and the formation of a residual film of adhesive of sufficient mechanical strength to hold the two surfaces together. This probably involves some type of electrostatic attraction between the joint surfaces and the adhesive. The theory which appears to fit the practical data best postulates the existence of fields of molecular attraction between the two materials forming the joint, which are superimposed on the ordinary cohesive force between the molecules of the substance in the thin film of adhesive. In some manner, at present unexplained, these molecular attractions are transmitted through a film of adhesive at least 100 molecules thick. Thus, this theory suggests a chain effect, whereby a large range of molecular attraction is artificially set up. The findings of a number of workers^{2, 124-129} appear to give support to this theory and in general specific adhesion accounts for the fact that the thinnest films give the strongest points. De Bruyne¹³⁰ considers that even in the wooden joints the adhesion is specific and points out that polar and non-polar forces exist between atoms and molecules so that strong joints can never be made to polar materials with non-polar adhesives or to non-polar materials with polar adhesives. Among polar materials occur water, alcohol, glycerol and normal wood whilst the non-polar group embraces benzene, paraffin, metals and heated wood. Objections to the polarity theory in the bonding of plastics have been raised by Halls¹³¹ and Mabain and Lee¹²² have shown that coumarin gives strong joints with both wood and steel, polar and non-polar materials, respectively.

It is possible that it is only when pure molten chemical substances which actually wet the materials in the true sense of the word are used to form a joint that both specific and mechanical adhesion come into play. If one of the materials is porous mechanical adhesion usually predominates, thus explaining the above-mentioned rough parallelism between joint strength and the strength of the film of the adhesive itself; other factors, such as the tensile strength, compressibility and the elasticity of the materials being joined, contribute in this case to modify the

weaker factor of specific adhesion. This theory may explain the value of adding a wetting agent to adhesives for joining smooth surfaces, in that the adsorbed air on the surface of the material is displaced by a solution of the adhesive and allows specific and mechanical adhesion to have fuller play than they would if the material were 'cushioned' with a layer of air.

A thick film of adhesive gives a weak joint because the strength of the joint is largely the strength of the adhesive itself, the joint surfaces being so widely separated that the forces of mutual attraction between them are relatively inoperative. Bikerman¹³² considers that two-thirds of the difference between the strength of thick and of thin films of adhesive can be accounted for by the greater probability of a weak spot occurring in a thick film, while the other third is due to conditions of formation of the film itself. With certain plastics thin films give joint strengths of high magnitude and the joint strength falls progressively with increase in thickness and finally remains approximately constant. Any weak points in a film have an overbearing effect on the joint strength so that their formation must be avoided. Keeping this in mind the porosity and the strength of the material will be seen to exert a strong effect on joint strength since the strength of a material generally increases with fineness of texture. This, in turn, regulates the speed of diffusion of the solvent through it. The solvent in a thin layer of film evaporates from or diffuses through the material more quickly and therefore the crystalline particle size or the size of the crystalline regions are more likely to be smaller than in the case of a thick layer in which crystallinity will be favoured and leads to spots of weakness. Evaporation and diffusion must therefore be taken into account more seriously with a porous than a non-porous material where evaporation occurs only at the joint edges and solvent from the interior takes a long time to escape.

According to Alexander¹³³ 'maximum adhesiveness corresponds to maximum colloidity'. Thus starch products which 'lie near but not quite in the zone of true crystalloid solution' are those which should exhibit the maximum adhesiveness and comparing the dextrans and alkali starches with dextrose we see that this is the case. Colloidal dispersions of starches have been examined by Houtz¹³⁴ whose work supports this explanation.

In spite of the amount of investigation that has been carried out on the subject not one of the theories advanced to explain adhesion phenomena appears adequate to cover every phase of the subject satisfactorily and a satisfactory, all-embracing theory has yet to be developed.

Another theory to account for adhesive action assumes that molecular forces operate over a much wider range than that allowed for in the older theories of physics, but this explanation is less attractive than the one set out above, and has many less experimental data to support it.

Flour Pastes.—In the Textile Section it is mentioned that certain flours are used to make sizes in preference to starches, because they are considered to possess greater adhesiveness. This superiority is explained by assuming that the presence of gluten assists the adhesive action. Some of the recipes given in the Textile Section may therefore prove of interest to those interested in the use of flour pastes for adhesives.

Flour pastes can be used *inter alia* as the adhesive for lining cardboard boxes with paper, affixing wall paper, bill-posting and labelling, bookbinding, and in the manufacture of paper goods of various kinds where the requirements are not too stringent. In general, flour pastes contain relatively little solid matter and consequently they show a tendency to dry slowly and sometimes to cause 'puckering' of the paper used; in this event adhesives with a higher solid-content must be used; for example, those made from treated starches or dextrans.

In the lining of cardboard boxes, cheap attaché cases or travelling trunks, an adhesive of the paste type can readily be used, and should be in the form of a very smooth paste quite free from lumps or any tendency to 'balling,' and its tackiness need not be pronounced. These pastes are also of value for the hand-labelling of bottles from which the labels are to be removed subsequent to use. For bottle-labelling by machine special types of dextrin adhesives are used. Pastes intended for use in affixing posters should be fairly weather-resistant and be tested for outdoor conditions. This test may be done by pasting a piece of the poster on to a brick or a board, drying slowly before a fire, and after wetting thoroughly by means of a fine spray of water, drying as before. A good poster paste should withstand several treatments without failing. Another property, which is preferable but not essential in a poster paste, is that of drying to give a fairly transparent film, so that coloured posters, or those with a black background, are not made unsightly with milky patches due to paste which has inadvertently become splashed onto the face of the poster.

Cereal flours generally form the basis of adhesive pastes; wheat flour and rye flour are those most favoured for a straight paste, but maize, barley and rice flours are also used. Very important is the stability of the pastes, which is assisted by the

addition of an acid, e.g. acetic acid. The water-holding power of a starch paste appears to be indirectly connected with its stability, and this property is usually determined when a new batch of starch or flour is received in the factory. A test that is used in a number of factories is as follows: The samples to be compared are made into mucilages of the same concentration and under exactly the same conditions. These mucilages are allowed to cool, and when they have gelled, a cylinder of the same size is cut from each and stood on end on a piece of filter-paper lying on a sheet of glass, covered with a bell-jar and left for several hours. At the end of this time the diameters of the rings of moisture on the papers are compared, and the comparison gives a good indication of the best flour or starch, as the one with the largest ring has the lowest water-holding power and therefore would give the least stable paste.

Finely ground tubers can be used for making pastes intended for rough work; the author has successfully employed tapioca tubers, some batches of which were badly diseased, for this purpose. In one case some difficulty was at first experienced owing to the very poor stability of the paste, which showed syneresis and breakdown in a few hours, but this defect was entirely overcome by the addition of a little bleaching powder before making the paste, the odour of the bleach being masked by the addition of a little oil of sassafras. It must be understood, however, that this type of product can only be used for very low-grade work, such as cheap board lining, and consequently commands a proportionately low selling price.

Generally, adhesive pastes are made with materials of good grade, and cleanliness throughout the whole of the processing should be one of the first considerations in the manufacture of first-grade products in order to prevent moulds developing on the surface of the finished product when it is stored in the factory. The temperature and time of storage of the pastes are also important. Pastes awaiting shipment should not be stored in such a position as to render them liable to freeze in cold weather, as on thawing, water rapidly separates from the paste leaving behind a crumbly, spongy mass quite useless as an adhesive (see Vol. I). To prevent fermentation of pastes containing nitrogenous compounds, Recries Française³⁸ pre-treats starchy flour containing nitrogen with a current of air or inert gas containing 0.1 to 0.2 per cent. of the oxides of chlorine. Antiseptics for starch products are dealt with elsewhere (Chap. 15).

Aluminium sulphate⁹⁹ and glycerine are two compounds frequently added to flour pastes to improve their properties.

The aluminium sulphate, besides acting as a preservative, also appears to increase the adhesiveness of the paste, and when this is dried exerts some influence on the moisture-resistance of the film. The glycerine is, as already mentioned, of value in preventing the film from becoming brittle and liable to fracture easily; besides rendering the film more pliable, it gives to the paste a smoothness in working properties.

Adhesives from Starch.—Starch forms the basis of a large number of adhesives varying from a simple paste made by heating starch with water to pastes made by complex processes entailing several treatments. Starch adhesives are used in many trades, and by making slight variations in the manner of carrying out a process, products widely different in character may be obtained. Using the same process, but varying the time or the temperature of the reaction, compounds are obtained which behave as thin-boiling or soluble starches at one end of the scale, and as thick, viscous and highly adhesive products at the other end.

Even the main starches of commerce, wheat, maize, tapioca, and potato, all behave in their own characteristic manner when submitted to the same process, the differences shown in some cases being truly striking, for example, those of the mucilages obtained by heating different starches with water. It is on these differences that the use of various starches for the preparation of sizes and dressing-agents for textiles is based. Starches processed in the same manner may yield products so dissimilar that they may be used advantageously for different purposes.

The starches most commonly used for the manufacture of adhesive pastes are potato and tapioca, and of these the latter appears more suitable in several respects. Tapioca starch gives adhesives which are more viscous, smoother in working and more easily prepared, whilst the joints made from them are considered by some to show a somewhat higher tensile strength than those made from potato starch. The bitter odour and taste of potato starch adhesives are also disadvantageous for some types of work.

The processes for preparing adhesives from starch, omitting those which give as end-products substances of a dextrinous nature or chemical derivatives of starch, may for convenience be classified under five main headings as follows :—

1. Treatment with caustic alkalis.
2. Treatment with other alkaline substances.
3. Treatment with acids.
4. Treatment with salts, oxidising agents or swelling agents.

5. Addition of various compounds to starch pastes formed by any of the above methods.

The effect of acids to produce dextrins and adhesives, and the modification of starch by means of oxidising agents, are dealt with elsewhere, and we shall consider them here only in so far as they are bound up with the other processes.

Of the straight starches used for producing adhesive pastes, tapioca, wheat and rye are perhaps the most widely employed and give the strongest and most adhesive pastes. Apart from certain lines of work indicated above, pastes made from starch and water without any special processing are not widely used, and we shall now pass on to consider the preparation of adhesive pastes by the methods outlined above.

Treatment with Caustic Alkalis.—The products obtained by the action of caustic alkalis on starch are known under a variety of names on the Continent; some of the names are mentioned in the Textile Section, and among other names are those of ‘colle universelle,’ ‘Collodine,’ ‘colle du japon,’ and ‘colle froid’.

By the action of caustic alkalis on starch, adhesives can be obtained giving joints with a strength practically equal to or greater than that of the materials joined. Such joints cannot be termed insoluble, but they are only difficultly soluble and resist moisture quite well. These pastes may be made by a cold process or by heating; those made in the cold are possibly not so stable as those made with heat because they tend to show some reversion.

In making cold adhesives the process may be carried out entirely at 15-20° C., and takes about 12 hours to complete. The mucilage may be neutralised either by the addition of an acid or a salt that reacts with the alkali, and sometimes with the starch as well. By using oxidising agents and heating the mass, soft, plastic and transparent adhesives are obtained, which will be dealt with later. The use of strong alkalis allows of the preparation of strong adhesives containing about 33-40 per cent. starch, which can replace dextrin adhesives for a number of purposes, and which are paler, cheaper, and capable of being diluted to a greater extent if necessary. In neutralising the alkali the process is generally allowed to finish slightly on the alkaline side, as this assists the stability of the paste, although it has a drawback in that it may give rise to staining when used with wood veneers; such preparations should not be heated when applying or drying.

Mérimée,⁴ as far back as 1827, mentions the advantage obtained by using a weak caustic soda solution for making a starch mucilage

for the sizing of paper. The first powdered preparation containing starch and caustic alkali, which when added to water gave an adhesive mucilage, appears to have been that patented by Marsden⁵ in 1888. Marsden mixed powdered ammonium sulphate with his mixture of starch and caustic alkali so that on the addition of water the alkali gelatinised the starch and was then neutralised by the ammonium sulphate to give the neutral metallic sulphate, whilst the liberated ammonia gradually passed into the air.

J. Kantorowitz⁶ appears to have been the next worker to take out a patent for the treatment of starch with alkalis. He treats the starch with caustic soda and after neutralising with hydrochloric acid precipitates the product either by adding magnesium sulphate or by keeping the mass at 20° C. for several hours. In a further patent he treats the starch with caustic soda in a concentrated solution of sodium sulphate. It should be mentioned that this treatment restrains the swelling of the starch and allows it to be readily separated from the liquor. Alcohol, acetone or mixtures of these with ether have also been used to obtain a similar effect.⁸⁻¹⁰

Simple as is the process of modifying starch with caustic alkalis, it appears to have been modified in approximately a dozen different ways. Leonhardt¹¹ pre-treats the starch with dilute acid prior to treatment with alkali, a process which is similar in principle to that used by Perkins¹² in America many years earlier. The contents of Perkins' original patents have been the subjects of much litigation; the process as claimed by him gives excellent products, having great adhesive powers and excellent appearance.

Perkins uses cassava starch and an equal weight of water, and pre-treats with 2-3 per cent. sulphuric acid at 55° C. for 4-6 hours. Any other treatment leading to the formation of a thin-boiling starch can be used instead of the above method, and Perkins himself has covered the use of sodium peroxide.¹³ The object of modifying the starch before making the adhesive is to produce a more fluid jelly, and a further method of achieving this end is to stir the jelly for five or six hours.¹⁴ The stirring is continued until a sample withdrawn from the batch flows thinly and evenly off a spatula or rod.

The adhesive jelly, which is used extensively in wood-veneering, is obtained from the pre-treated starch by running into a slurry of practically equal parts of starch and water about 15 per cent. by weight of a 33 per cent. solution of caustic soda. More water can be used to suspend the starch if desired, but this will naturally lead to a final product having a lower solid-content and different adhesive strength. In this process the higher the temperature

of the conversion, the less the amount of caustic soda required to bring about the required change.

The appearance of the mass changes quite suddenly at a certain point during the addition of the caustic solution; the white and extremely tough leathery mass first produced suddenly changes to a colourless jelly as the addition of the caustic is continued.

The old formula for the preparation of wood veneers, i.e. 1 pt. of tapioca starch to $2\frac{1}{8}$ pts. water, was not entirely successful because, owing to the presence of the comparatively large amount of water present, the adhesive penetrated too deeply, causing weak joints (see p. 131). As previously stated, Perkins uses sodium peroxide to modify his starch before making the paste to obtain a more fluid product and thus allow a reduction to be made in the amount of water used. Another method¹⁰⁰ is to add barium peroxide and urea to the starch before making the paste, the urea stabilises the glue and tends to retard the evaporation of the moisture. The quality of the pastes made in the above manner improves with increasing concentration of the starch, with the efficiency of the stirring, and the rigid maintenance of the temperature throughout at $15-20^{\circ}\text{C}$.

The following formula will serve as a guide to the making of a paste of this type: 84.4 pts. tapioca starch, 0.5 pt. barium peroxide, 0.1 pt. soda ash, 5 pts. whiting, and 10 pts. urea are well mixed, and 100 pts. of this glue base are heated with 120 pts. of water to 70°C . The addition of 2.5 pts. of caustic alkali is made in the usual manner. Using this method, sago, maize or even potato starch may be used to give a good veneering adhesive.

The addition of about 1 per cent. of potassium dichromate and of calcium peroxide to a starch base before forming the glue allows the use of a lower temperature and of less caustic alkali. The calcium salt is thought to improve the water-resistance of the joint. If desired, the potassium dichromate can be replaced by potassium pyroantimonate. Ferrous sulphate is also used as a catalyst.¹⁰¹ In a recent patent by Perkins the viscosity of the final glue is brought within desired limits without any acid pre-treatment, to which reference has been made, by adding to the starch base a small amount of a copper salt to act as a catalyst to the action.

A very good adhesive may be made by suspending 150 pts. starch in 100 pts. water and adding 25 pts. caustic soda solution (36°Bé.) diluted with an equal volume of water, and stirring the mass for 60-90 minutes at a temperature between 15° and 20°C . If it is desired to neutralise one of the above pastes, the acid used should be but slightly diluted; thus, to neutralise and dilute

a paste to a desired water-content the bulk of the water of dilution should be added first, followed by the acid diluted with a small amount of water, rather than the acid added to the whole of the water and then this added to the mass. A typical formula for a very slightly alkaline starch is the following: 140 lb. starch are suspended in 210 lb. water and 35 lb. caustic soda liquor (36° Bé.) diluted with 35 lb. water are added with constant stirring. When the mass 'comes across,' i.e. is thoroughly converted, 550 lb. of water, in which is dissolved 0.14 lb. borax, are slowly added, followed by 5 lb. hydrochloric acid (22° Bé.) diluted with 50 lb. water. If the alkali present is exactly neutralised, the viscosity of the resulting paste is lower, and it is preferable to omit the borax and slightly increase the starch/water ratio, as the thickening action of the borax is lost under these conditions.

According to Gröninger,¹⁵ pre-treatment of the starch with triethanolamine allows a very smooth alkaline conversion to be subsequently carried out, minimising the formation of lumps resistant to the processing. Supf¹⁶ obtains a dry powder capable of giving a viscous adhesive by treating starch with an equal amount of caustic soda solution (36° Bé.) at a few degrees above 0° C. Very little swelling of the starch takes place at this temperature, and what swelling does occur causes the absorption of all the water present. The practically dry powder is then freed from alkali by washing with alcohol. Both the alkali and the alcohol in this process are recovered and used repeatedly. Among other attempts to obtain dry products are those of Pfeiffer and Schwander,¹⁷ who spray caustic liquor of the same strength as that used by Supf on to potato starch which has been mixed with an organic liquid. Some 25-30 kg. of solution are used for 100 kg. starch. H. Bechhold¹⁸ employed a somewhat similar process, but specifies that the organic liquid shall be insoluble or only slightly soluble in water. The use of chlorinated hydrocarbons or of hydroaromatic alcohols and ketones is excluded. He employs 3 per cent. of benzaldehyde on the weight of starch and dries the product at 50-70° C. O. Meyer¹⁹ claims the use of cyclohexanone. He treats starch with 3 per cent. of cyclohexanone followed by aqueous caustic soda, the final paste being neutralised with oxalic acid. The paste obtained is white and very smooth and can be used for paper-lining work. Neutralisation of an alkaline starch paste tends to destroy the 'ropy' character of the paste, which becomes smoother and more 'bland'.

F. Riethof²⁰ mixes 3 per cent. amyl alcohol or 3.5 per cent. aromatic amine with the starch before the treatment with caustic and modifies the product so obtained by adding an acid, such as

oxalic acid, or an acid salt, such as sodium bisulphite. The use of a chlorinated hydrocarbon is claimed by the Sächsische Klebstoffwerke²¹ for the same purpose, the decomposition in this case being carried out by heating the mass to 30-35° C. for 25-30 minutes.

Henkel et Cie²² consider that the use of these organic liquids leaves much to be desired and that organic liquids soluble in water should preferably be used. They employ an emulsion of trichloroethylene, some 4-5 litres being sprayed on to 100 kg. starch before treating it with 26.5 kg. caustic soda solution of sp. gr. 1.332.

The following formula gives excellent results with tapioca starch, and can also be used with potato starch, but in the latter case the resultant jelly gum is more adhesive although less stable, and more difficult to treat: 320 lb. tapioca starch are suspended in 500 lb. water in which is dissolved 0.65 lb. sodium bicarbonate; 80 lb. caustic soda liquor (36° Bé.) diluted with an equal weight of water are slowly run in and stirred for 12 hours at a temperature between 15° and 20° C. At the end of this time 38 lb. acetone are added followed by 6 lb. formaldehyde solution (30 per cent.) and 0.65 lb. ammonia-finished turkey-red oil; after stirring for a further 20 minutes at not too fast a rate the batch is run off.

In order to obtain a dry product, various workers have treated starch with dry caustic alkalis,²³ followed by the addition of a powdered solid organic acid.²⁴ Mahler and Supf²⁵ grind 100 kg. starch with 5-6 kg. powdered caustic soda and neutralise with 6-11 kg. of powdered oxalic acid. On adding water, these products swell but have the drawback of usually forming lumps which are difficult to convert into the paste form; to overcome this, Henkel et Cie²⁶ grind in the presence of a little water and then dry and re-grind. Another method^{27, 28} of conducting this process is to grind the starch with the dry alkali, then add moist starch, re-grind and dry. Better results are obtained if the starch added after the preliminary grinding is moistened with a mixture of alcohol and water. Pfeiffer and Schwander²⁹ treat starch with finely-divided alkali solution to which is added 10 per cent. of a water-soluble, volatile solvent to assist the drying process. To obtain a product free from any trace of colour, to be used more especially for the sizing of white goods rather than as an adhesive, Leonhardt³⁰ decomposes starch with alkali *in vacuo*, and when the modification is complete, passes ammonia or sulphur dioxide through the mass to destroy the colour. The product in this case is also a dry powder.

Treatment with other Alkaline Substances.—Milder alkalis

may be used for the modification of starch, and patents have been taken out covering the use of a number of these compounds under varying conditions. According to one,³¹ a paste similar to that obtained from wheat starch may be made by acting on potato starch with a solution of a mild alkali containing certain additions, such as alkaline persalts, peroxides, or neutral persalts. The starch is modified by this method to give a product approaching that obtained as soluble starch; for example, 100 kg. of potato starch are suspended in water to which is added from 0.5-2 kg. ammonium persulphate and 1 kg. ammonium hydroxide of sp. gr. 0.88. The product obtained from this conversion is a soft, lard-like, adhesive paste.

A painters' glue can be made from paste-like products that are obtained by modifying the starch with alkaline-earth compounds in the presence of such amounts of alkali compounds as are capable of being transformed by the alkali-earth oxides to alkali hydroxides in a concentration less than 2 per cent.³² The following example illustrates this process: 100 kg. starch are treated with 14 kg. of sodium silicate (36° Bé.) and 4 kg. slaked lime. For the preparation of the painters' glue the results obtained by the above process are improved if a little rosin soap is added to the starch suspension and the modification carried out at room-temperature. Using only concentrated solutions of alkaline-earth hydroxides, Runge produces swelled starch by heating the mixture, and after swelling has taken place, neutralising the alkali present with a solid acid, e.g. oxalic acid. In Runge's process,³³ 1 pt. of starch is heated to 70-80° C. with 3 pts. of a saturated solution of calcium hydroxide; after drying, the mass is ground with the requisite amount of oxalic acid to neutralise the alkali present.

Products which on drying split off alkaline hydroxides hydrolytically, but yet in solution have little swelling action on the starch, can be used to produce dry products of value as adhesives.³⁴ The adhesive qualities of the pastes may be regulated by controlling the amount of the alkali-producing substance added. Soda lime, sodium silicate and aluminate, etc., are among the substances used in this process. Paste-like products may be formed by the addition of water to the substance produced by the action of less than 30 per cent. sodium silicate on the weight of starch. To obtain this product, 200 kg. starch are suspended in 175 litres of water, and 60 kg. of sodium silicate (30° Bé.) are added. The mixture is dried on hot rollers and then ground to a fine powder. If glue-like products are required, the amount of silicate is increased until it exceeds 30 per cent. of the weight of

starch. An additional patent substitutes the above-mentioned materials by barium hydroxide.³⁵

In a further patent³⁶ the decomposition of starch to obtain adhesive pastes is carried out with alkali salts of weak inorganic acids, e.g. borates, aluminates or stannates, which have no influence on the starch at ordinary temperatures but cause it to swell on heating. Haake³⁷ neutralises a solution of borax with chlorine at 40° C. and suspends his starch in the solution until the particular modification required is obtained. The product is washed and dried, and gives thin-flowing solutions containing a high percentage of starch, which can be used either for sizing or for adhesives.

One outstanding advantage obtainable by the use of weak alkalis by any of the above methods, is that the reactants can be more easily mixed in with the starch than can strong alkalis, and little or no action takes place in the cold; but when the batch is ready the temperature can be raised and good homogeneous pastes obtained.

A number of products are obtained by first forming an alkali starch and then treating the solution with an alkaline-earth compound, which precipitates the alkaline-earth starch. In place of the alkaline-earth hydroxides, heavy metal salts, such as barium chloride, may be used and the resultant precipitate separated and dried.³⁹ By mixing this powder with a water-soluble alkali salt, such as sodium sulphate, a cold-water swelling starch is obtained which gives adhesive pastes on the addition of water.⁴¹ The precipitate obtained by treating alkali starch with an alkaline-earth compound may be treated with reagents to obtain derivatives containing barium, calcium, strontium, beryllium, magnesium, zinc, aluminium, iron, copper, or double compounds containing two of the above metals. The copper compounds obtained by this method are said to have disinfecting properties.⁴⁰

The above compounds may be treated with chlorine and the chlorination followed by a treatment with an acid gas; the products obtained in this instance, however, are soluble starches. Magnesium chloride or calcium chloride may be used in the production of adhesives, that produced from magnesium chloride giving a very adhesive paste which is useful for paper work, or as an agent to carry the filler used in paper surfacing; when used for the latter purpose it shows very little tendency to absorb atmospheric moisture. The calcium chloride process is now fairly well known, and good adhesives may be obtained by treating 100 pts. of starch with 50 to 100 pts. of a highly concentrated calcium chloride solution at room-temperature or

slightly above it, and adding to the mixture 50 pts. of animal glue to increase the 'pick-up' or adhesiveness. The mass is ground and dried and the powder so obtained dissolves readily in water to give an adhesive mass.⁴²

Treatment with Acids.—Lintner made a soluble starch by acting on potato starch with 7·5 per cent. hydrochloric acid for several days at room-temperature. The modified starch gives a clear solution in water, but if a starch other than potato starch is used the solution is opalescent. The maximum action in the above case takes place during the first day and after 30 days the starch has undergone but slight further change.¹⁰³ The phosphorus-content and viscosity change but little during the last 29 days, and one-day and thirty-day products react in the same manner when treated with β -amylase. At the end of 30 days only about 4·5 per cent. of the starch dissolves in the hydrochloric acid solution.

When 15 per cent. hydrochloric acid solution is used the results are very different, in that with continued action greater amounts of starch go into solution in the acid, until after 30 days some 60 per cent. has dissolved. The viscosity decreases but little after the first day, but the phosphorus-content decreases progressively. In this reaction a fraction insoluble in hot water begins to form after the tenth day and increases in amount progressively with the length of time of treatment. It appears to be similar to amylo-hemicellulose, contains 1·3 per cent. ash, traces of phosphorus, but much silica. The dextrin in the acid solution can be precipitated with alcohol, gives a reddish-brown iodine reaction, and has a higher phosphorus-content than the original starch.¹⁰³ The use of a soluble starch made by the action of 15 per cent. hydrochloric acid on potato starch for 6 days has been suggested for the determination of the activity of malt extract in place of Lintner starch. The effect of cold dilute acids on starch has been studied in great detail by M. Samec¹⁰⁴ (see also V. I. Nazarov¹¹¹).

One of the earliest processes for treating starch with acids is that of J. Sellars⁴³ who, in 1865, neutralised the mass with soda after the acid treatment. By the action of vegetable and mineral acids starches may be modified so that their solutions range from mobile liquids to viscous and adhesive pastes. Some early treatments⁴⁴⁻⁴⁶ involved heating the starch under various conditions of temperature and pressure with sulphur dioxide.

The 'in suspension' process is widely practised and embraces most processes in which a starch is suspended in a dilute acid solution and maintained at a temperature varying from room-

temperature to just below that of the gelatinising point of the particular starch being processed. Such starches appear to be unchanged visually, but readily go into solution in hot water or dilute alkaline solutions. Klopfer⁴⁷ mixes rice starch with 0.5 per cent. lactic acid, and at the end of the treatment centrifuges it and dries the product. H. H. Lake⁴⁸ treats the starch with strong hydrochloric acid and dries at a low temperature, the product obtained being a thin-boiling starch. Duryea⁴⁹ suspends starch in a 1-2 per cent. aqueous sulphuric acid and maintains the temperature at 45° C. for 1 to 4½ hours; when the required modification has been effected the acid is neutralised, filtered off, and the product dried. Bergquist⁵⁰ adds hexamethylenetetramine or formaldehyde during this treatment and heats to 72° C. to obtain a product which gives a perfectly clear film on drying. Such a product may be used as an adhesive in, for example, poster work, where transparency of the dried paste is a desirable feature. Murphy⁵¹ suspends starch in dilute sulphuric acid and passes in superheated steam until the mass liquefies, when the passage of the steam is discontinued, the acid neutralised with chalk, and the mass filtered hot. Browning and Barlow⁵² spray hydrochloric acid on to dried starch maintained at 45° C.; B. Helferich and his co-workers⁵³ use anhydrous hydrogen fluoride at 20° C. and after 30 minutes remove the acid with a current of air. In later patents^{54,55} both starch and cellulose are treated in this way, the temperatures ranging from room-temperature to 90° C. H. Schenbach⁵⁶ treats starch with gaseous hydrochloric acid under pressure in the presence of an organic liquid, such as benzene, which is removed at the end of the process by filtration. Stutzke⁵⁷ sprays a starch suspension, which may contain acid, into a current of superheated steam or, according to another patent, a mixture of starch and water may be sprayed into hydrochloric acid vapour in a chamber at 200° C. In the latter process the starch is modified and dried simultaneously, as in this medium the partial pressure of the water vapour corresponds to the boiling-point of water at 32.5° C. Again, a wheat-starch suspension may be atomised in a chamber containing air at 300° C. at a pressure whereat water boils slightly above the gelatinising temperature of the starch. A number of other patents cover the treatment of starch by spraying with a small amount of acid, heating until the required stage is reached and then drying it on hot rollers. Methods embodying this principle effect great saving of time, labour and power.

The conversion of starch by means of acid either by the wet method or by dry heating is dealt with more fully in the chapter

on Dextrin, and the reader is also referred to the section on Ethers and Esters of starch, especially to those portions dealing with the acetates and the xanthates, both of which are used commercially as adhesives.

Treatment with Salts.—In the preceding pages the use of certain salts like magnesium or calcium chloride for obtaining starch pastes has been mentioned, and we may now consider further the various uses to which metallic salts are put in the adhesives industry.

Several workers^{61, 62} have examined the effect of salts at different concentrations and at various temperatures on the swelling and gelatinisation of starch and, as will be seen, their results have found practical application. Courtonne,⁵⁸ for example, found that chlorides exerted most effect on the gelatinisation point, whereas sulphates exerted a retarding action. Thus we have the preparation of adhesive pastes like that of Möller-Holtkamp,⁵⁹ who treats a thick paste with calcium chloride and reboils the mixture, or the patent of Alexander,⁶⁰ who uses a high concentration of the salt to swell the starch. Mention has been made (see p. 141) of the addition of sodium sulphate to reaction mixtures to prevent swelling and gelatinisation taking place, thus allowing easy filtration and handling of the treated starch.

The effects of salts in general upon starch has not received the same amount of academic attention as that of acids and bases, and the number of references in the literature is correspondingly small. It is now generally known, however, that certain salts have the power of dispersing or liquefying starch paste, or even gelatinising the raw starch when applied in concentrated solution. The value of this phenomenon in the study of the structure and physical chemistry of starch has been discussed in full in Vol. I. Salts have three main uses in adhesive work: they may be employed as swelling agents, as stabilising agents, and to impart transparency, adhesiveness, density or to increase the viscosity of the paste.

E. Meusel,⁷² sixty years ago, noted that various thiocyanates, potassium acetate and calcium chloride in solution gelatinised starch at ordinary temperature and that the concentration of the salt plays an important part in the process. Small quantities of certain salts, even in concentrations as low as they occur in tap water, have been found by L. Eynon and J. H. Lane⁶² to affect the viscosity of starch pastes adversely. With soluble starch an effect particularly noticeable is the regaining of gelatinising power if ordinary hard water is used to wash it during its preparation. This is explained by D. R. Nanji and R. G. L. Beazeley⁶³ by

postulating the absorption of calcium to form the calcium salts of the amylophosphoric esters which constitute the amylopectin portion of the starch (see Vol. I).

Commercially, however, a number of processes have been covered by patents and have as their object the production of starches which swell or dissolve in cold water, or the preparation of adhesives.

One of the first patents covering the use of salts for modifying starch was taken out by the Arabol Manufacturing Co.⁶⁴ In this patent, starch is heated with a strong solution of potassium or ammonium thiocyanate in alcohol, e.g. 100 lb. potato starch are added to 80 lb. of a 50 per cent. solution of ammonium thiocyanate containing 40 lb. of alcohol.

Neustadt⁶⁵ recommends treating 100 kg. of potato starch with 3 kg. of calcium nitrate, 1.5 kg. of sodium chloride, and 1.5 kg. magnesium sulphate, the mixture being ground after the solutions have been added to the starch. The swelling action of calcium chloride solution on starch is well known, and Wattecamps,⁶⁶ by mixing starch with its own weight of a concentrated solution of zinc chloride containing sodium chloride, obtains, after the mixture has been standing some time, a hard, gum-like mass which is soluble in cold water. According to his specification, 2,100 gm. zinc chloride, 250 gm. sodium chloride, 1,375 gm. calcium chloride and 125 gm. ammonium chloride are dissolved in 3,475 gm. water, and to the solution 2,000 gm. rice starch, 800 gm. potato-starch flour, and 500 gm. white dextrin are added.

A very transparent and syrupy paste may be prepared by suspending 100 lb. starch in 180 lb. water at room-temperature and adding 115 lb. calcium chloride to the suspension with constant stirring, which is continued for two hours. To increase the viscosity about 1 lb. borax may be added at the end of the process. This preparation offers no difficulties and special precautions are unnecessary. Adhesives of this type, containing more water, are widely used in the manufacture of wallpapers, as the binder for surfacing pigments, metallic powders, etc., and magnesium chloride in equivalent amounts may also be used with excellent results for this type of work. R. Dulac⁶⁸ has found that the consumption of calcium chloride can be reduced by 13-15 per cent. if about 2 lb. of alum is included in the above formula. If borax, however, is used, more water and calcium chloride are required to obtain a paste of the same fluidity.

R. L. Datta and co-workers¹⁰⁸ have described the preparation of fluid office pastes and find that potato starch gives the best effect for this type of adhesive. The formulæ they give work

well and are satisfactory for general office work. The starch, 100 pts., is sifted into 70 pts. of water containing 36 and 47 pts. of zinc chloride and calcium chloride, respectively, at a temperature of 65° C. The liquid is stirred during the addition of the starch and thickens to give a clear translucent gel which is then diluted with 800 pts. of hot water. Maize and wheat starches can be used but are not nearly so satisfactory as potato starch.

Kühl and Soltan⁶⁷ use neutral persalts to obtain strong adhesives with a glassy appearance; for example, they treat rice starch with 1 per cent. of a persalt, such as ammonium persulphate or sodium perborate, for 7-8 minutes at 3-5 atmospheres' pressure. Ninety-six parts of starch and 4 parts of ammonium persulphate heated together for 2-3 hours at $45\text{--}50^{\circ}$ C. give a good cold adhesive.

Stein⁶⁸ obtains modified starches and adhesives by treating starch at elevated temperatures with 1-2 per cent. of salts, such as potassium iodide, aniline, hydrochloride or organic sulphonates, the products giving homogeneous pastes with cold water.

One feature of certain powders that swell in contact with moisture is that they form lumps when added to water. In some cases the powders have to be sifted onto the water, which is stirred during the addition, but even then small lumps are apt to form and give rise to a heterogeneous paste. J. Kantorowitz⁶⁹ has overcome this difficulty in the case of certain soluble starches by mixing the starch with a salt, e.g. alum or magnesium sulphate, which exerts some wetting action but retards the swelling. The effect of these salts in retarding the swelling action is also made use of in the manufacture of modified starches, the starch being processed in their presence and a product obtained which is easily handled.

Another patent, granted to Mahler and Supf,⁷⁰ although not coming strictly within this section, may be mentioned here owing to the similarity of some of the claims to those in the Kantorowitz patent. They add two kinds of materials to prevent lumping, (a) thickeners for starch pastes, such as alum, weakly alkaline reacting materials, tannic-, fatty- and resinous acids; (b) compounds which can precipitate starch from its solutions, principally magnesium compounds. These additions can be made to the starch or to the water. In a further patent⁷¹ the same workers claim the use of soluble albumins, gums, dextrans, and pectin in the same manner.

Borax is widely used in the adhesive industry and particularly for adhesives containing dextrin. If borax is added to a starch

paste the mass becomes like rubber and cannot be spread because it 'balls up' on the surface to which it is applied, in other words, it crumbles into little rounded masses while being spread. If the paste to which the borax has been added is treated with an acid, a workable paste is again obtained. One of the chief uses of borax is in the preparation of laundry stiffening mixtures; by stiffening the finished film it allows a higher glaze to be imparted by ironing or calendaring.

Henkel et Cie⁷³ use this property to obtain thicker solutions from the starches soluble in cold water that are obtained by grinding starch with caustic potash, water and alcohol,²⁸ and they also employ calcium borate⁸⁷ for the same purpose, except with the soluble starches made by the action of calcium halides. After obtaining calcium starch, this firm treats it with an alcohol-water mixture which eliminates the calcium and gives an adhesive product.^{74,75} In another patent these calcium preparations are also treated with borax to solubilise them and produce adhesive pastes.⁷⁶

In one patent, Grosvenor⁹⁶ employs trisodium phosphate, tribasic lead acetate or sodium aluminate, substances which have already been mentioned as being used in the preparation of adhesive pastes.

Borax can be used with lower-grade starches to make pastes with a higher viscosity than could otherwise be obtained, amounts of 1-2 pts. of borax to 1,000-10,000 pts. of starch effecting a notable increase in viscosity, the effect being greater the more nearly the reaction of the paste approaches neutrality. In a neutralised alkali paste, salt is added to increase the density. The addition of calcium chloride to such pastes renders them somewhat turbid and less viscous, and introduces the factor of hygroscopicity; and the same applies to the addition of magnesium chloride but to a more marked degree. The amount of sodium chloride added may vary widely for different purposes, between such limits as 10 to 50 per cent. on the weight of starch, leading to a great improvement in transparency, ropiness and density, but retarding the drying of the paste and giving low water-resistance. Such a paste can be diluted considerably and is quite stable, but is, of course, not meant to be employed for high-strength joints.

Dense and opaque adhesives which may be readily diluted with water, and are cheap, may be made by introducing sodium silicate into the formula. Such an adhesive may be made by suspending 130 lb. tapioca starch in 20 galls. water, adding 33 lb. caustic soda (36° Bé.) diluted with 3.3 galls. water, and after forming the alkali starch, diluting with a further 20 galls.

water. To this solution is added 43 lb. sodium silicate solution (35° Bé.) and 0.1 lb. borax dissolved in 15 galls. water, and the mass stirred until homogeneous. The mass is next practically neutralised by the addition of 35 lb. hydrochloric acid (22° Bé.) and diluted with 20 galls. water, which are added slowly and with constant stirring. The final addition is made of 1 gall. formaldehyde (15 per cent.). The paste so obtained is slightly alkaline and thus allows the borax to exert its maximum effect as stabiliser for the precipitated silica gel. It may be, however, that the alkaline nature of the finished product is undesirable, and then the water-content is kept lower, and the borax replaced by a little alum, which assists in neutralising the residual alkalinity and also increases the viscosity and water-resistance of the paste. Pastes made with sodium silicate are 'ropy,' and no work appears to have been done concerning its effect on the tensile strength of the joint made with such an adhesive. Most neutral salts increase both the viscosity and the density of the paste; although they generally stabilise the paste, there always remains the fact that they have no adhesive power of their own, and therefore their use leads to the production of weaker joints. Their tendency to increase the hygroscopic nature of the paste should also be considered in formulation. The compactness obtained by some salts can be obtained in several cases by the use of quite a small amount of soap.

Treatment with Oxidising Agents.—We have already dealt with the general effect of oxidising agents, used alone, upon starch, but if the action is modified by being carried out in the presence of an alkali the reaction can be stopped at a point at which the products obtained are not thin-boiling starches but adhesives that are cheap, rapid-drying and efficient. These adhesives may contain as little as 8 per cent. or as much as 50 per cent. of starch, and the joints obtained by their use are said to be excellent in their moisture-resisting properties.⁹⁸

Tapioca starch is used, but potato starch may replace it if a somewhat inferior product is allowable. A feature of this process, as distinct from the manufacture of glues using strong alkalis acting in the cold, is the employment of higher temperatures, and the inclusion of formaldehyde, which appears to exert a specific effect on the finished joint made with such adhesives.

If adhesives with a solid-content in the upper range are required, more oxidising agent must be used. Thus for a paste with a water-tapioca starch ratio of 8-1, about 0.02 per cent. of 12-volume hydrogen peroxide is required, for a 6-1 ratio about 0.035 per cent., for a 3-1 paste about 0.35 per cent., whilst for a 2-1

ratio the amount used rises to 0.8 per cent. Hydrogen peroxide has the advantage over metallic hypochlorites of leaving no residue after the reaction. To make these adhesives, 1,000 lb. of starch suspension of the required solid-content is made containing 6 lb. of lime or 0.45 lb. caustic soda liquor (36° Bé.), the hydrogen peroxide added and the temperature raised to 80–85° C. A strong reaction takes place; further reaction may be observed when a little formaldehyde is added to the paste while hot, a small amount of formic acid being formed which assists in neutralising the paste. When the water-starch ratio is 3-1, calcium chloride to the extent of 3.7 per cent. is added before the formaldehyde, and with a 2-1 ratio, lime is used in preference to caustic soda when the suspension is first made. The addition of 0.05 lb. of Marseilles soap to the suspension before heating gives a smoother paste. The solutions obtained as above should be quite watery when hot, and on standing should give a smooth lard-like paste.⁹⁸ A paste with a 3-1 ratio, or a 2.5-1 ratio, forms a valuable adhesive for cigarette papers or other thin paper, where the inclusion of too much water would induce puckering. Such pastes are also free from the defect of giving a brownish stain down the cigarette, and from the smell and taste of burnt sugar given by many dextrin adhesives. Here again potato starch may be used instead of tapioca starch, but such pastes have the usual strong odour associated with potato starch. In this case the alkali used is sodium zincate, formed by the reaction between caustic soda and zinc sulphate, and the proportions in which these two substances are used determines the properties of the finished paste; the greater the amount of zinc sulphate used, the whiter the paste and the lower its final viscosity.

N. A. Spasski¹⁰⁹ makes a bookbinding paste using bleaching powder and a potato or maize-starch suspension, but his formula has no new features.

Treatment of Starch with Swelling Agents.—We have considered several metallic salts which have the power of swelling starch and may now turn our attention to other compounds possessing a similar action.

Mauch,⁷⁷ and Schulze,¹⁰² and Schaer⁷⁸ have examined the swelling action of chloral hydrate on starch. This compound exerts a very powerful effect and, as previously stated, it behaves similarly in presence of gelatine. Henkel et Cie claim the use of this compound in one of their patents.⁷⁹ They make the starch swell by treating it at a high temperature and pressure with urea, or thiourea, chloral hydrate, etc., in the presence of small amounts of liquids miscible with water, e.g. 100 kg. starch

is treated with 2 kg. urea and 10 kg. alcohol and the mixture heated at 170° C. under 500 atmospheres' pressure. Still another patent covers the use of water-immiscible amines and chloral hydrate.⁸² E. F. Hoppler and J. W. Haake⁸⁰ heat various starches, grains, or tubers containing less than 25 per cent. moisture with urea, chloral hydrate, thiocyanates, calcium halides, or numerous other specified modifying agents, at the same time subjecting the mass to mechanical pressure.

Reference should also be made to Vol. I, where a number of agents which could be used in this manner are listed.

Addition of Various Compounds to Starch Adhesives.—

Mention has already been made in previous sections of a number of compounds added to starch preparations to improve the working properties in one direction or another. It is extremely doubtful if one adhesive will ever be discovered that can be used to solve all the many problems in the adhesive field, for the property which has outstanding value in one set of circumstances may prove to be as big a drawback in another.

Various modifying agents are added to starch adhesives to render them suitable for specific purposes. To control consistency borax, soda ash or methyl cellosolve are added: to increase the water resistance much recent work has been directed towards the incorporation in starch pastes of the water soluble components or the water-soluble precondensates of urea-formaldehyde and melamine-formaldehyde resins whilst the addition of formaldehyde or formaldehyde generators has long been practised. The addition of wetting agents, soaps, resins, protein glues and rubber latex so alter the properties in characteristic fashions as to give greater penetration, maximum spread and greater tack.

Plasticising agents modify the film of adhesive so as to improve its deformability and hence its strength (see p. 132). Some of the more common compounds mentioned in the patent literature as useful in this respect are glycerol and glycols, urea, sorbitol, castor oil, sodium acetate or lactate, lactic esters, sodium nitrate and alkali thiocyanates. Care must be taken in the addition of plasticisers to avoid proportions which will lead to crystallisation or exudation by syneresis.

According to Kirkpatrick¹¹⁵ plasticisers function in at least 3 ways: (1) by solvent action of the adhesive material; (2) by simple lubrication of the molecular layers, and (3) by a combination of these actions.

We thus find it necessary to add various compounds to a certain preparation so that from one base several adhesives for different classes of work may be obtained. Special types of adhesives show

definite drawbacks, not so much in their use but in their preparation, and this applies also to the dextrin adhesives. Thus one drawback to a certain type of adhesive, which is sold in the powder form and has to be dissolved in water before use, has already been mentioned as consisting of the formation of clumps of material which are very difficult to get into solution unless adequate facilities for heating, mechanical stirring, etc., are present, and often they are absent.

To overcome this tendency to form lumps on addition to water, the Jagenberg-Werke⁸¹ treat the adhesive powder, in this case a dextrin, with a small quantity of a polyhydric alcohol, preferably an aliphatic glycol such as ethylene glycol, and heat the mass to about 80° C. The powder obtained goes into water quite smoothly and only about 1 per cent. of the agent is required. When dry, inorganic fillers are to be used in an adhesive they should first be pasted with water, preferably containing a little soap, to prevent the formation of lumps.

The addition of urea has already been briefly indicated, and it is interesting to note that this compound is used in the manufacture of adhesives from casein, gelatine or glue as well as from starch. The viscosity of the solutions is reduced so that the content of solids may be increased and the same working consistency obtained as when no agent has been added and the original solid-content employed. With paper adhesives this tends to stop the crinkling of the paper, or the splitting of paper which has been stretched during the application of the adhesive, when the joint dries, as often happens when a paste of a high water-content is used.

Besides lowering the setting- or gel-point of the adhesive paste, urea is claimed to increase the tensile strength of the joint.⁸³ It is especially useful in certain classes of work in which paper is used or where non-rigid joints are required.

As urea stops the 'set-back' of adhesive pastes it forms a useful stabilising agent and, as before mentioned, its use allows a reduction in the degree of oxidising action or the amount of alkali and processing necessary for attaining a certain fluidity. It has a further peculiar action in retarding the initial evaporation of water from the glue. It does not interfere with the quick-setting action required in certain adhesives once this has started, and which is brought about by the use of less water, but it appears to delay the inception of the quick-setting action. This property has been found particularly advantageous in the preparation of glues for plywood, bentwood, and veneers. The insoluble products

obtained by the action of formaldehyde on starch, described elsewhere, can be solubilised by the use of this agent, and thiourea would probably be quite as effective, if not more so, but its greater price would prohibit its use on economic grounds. H. F. Bauer¹⁰⁷ has covered the use of about 5 per cent. of urea and 5 per cent. alkali metal acetates in re-moistening adhesives.

Thick pastes with smooth-working properties for paper work are obtained by the addition of a soap which acts as a thickener and gives the paste an unctuous consistency. A 10-12 per cent. starch paste containing 0.5 per cent. caustic liquor (36° Bé.) gives a good paste if 1.2-1.5 per cent. of soap is added before heating. If a low-grade starch which tends to be thin-boiling is used, the caustic soda solution may be replaced by 0.03 per cent. borax, which will body it up. By the use of hydrogen peroxide a higher ratio of starch to water may be obtained, the soap being added to the paste after the action of the peroxide is nearly complete.

Of recent years a remarkable class of compounds has been developed, chiefly for use as detergents in the textile industries and to 'wet out' textile fibres. The addition of a small amount of these wetting agents to aqueous solutions assists the solution to displace the top layer of air on a given surface, thus allowing the liquid to make contact with the substance. When one considers the difficulty of wetting certain foils used as wrappers or waxed papers, highly calendered surfaces, etc., the value of these agents for use in adhesives will be appreciated. Many of them are stable to acids, salt solutions, and hard water, thus further increasing their usefulness.

In one patent the products obtained from the action of sulphuric acid on the alcohols obtained from tallow, coconut oil, castor or sperm oils, are added to potato-starch pastes to improve the spreading properties of the pastes. For potato-starch pastes the sodium cetyl sulphonate, in amounts varying from 1-3 per cent., may be used. W. Schrauth⁸⁴ claims the use of 0.5-5.0 per cent. of the reaction products obtained from sulphuric acid and an aliphatic or cycloaromatic, saturated or unsaturated, alcohol containing eight or more carbon atoms. Henkel et Cie⁸⁵ use certain wetting agents stable to lime in the proportion of 0.1-1.0 per cent. on the dry base. The agents they claim may have in the molecule a long-chain alkyl group, or hydroaromatic group and a sulphonic, sulphuric ester, phosphoric ester, carboxylic, quaternary ammonium, ether or aminosulphonic group; for example, sodium dodecyl- α -sulphonate, disodiummethyl sulphate, or compounds of the formula $R \cdot O \cdot CO \cdot CH_2 \cdot S \cdot SO_3 \cdot Na$, where

R stands for C_8H_{17} or its immediate higher homologues. To increase the smooth-working properties of cold-water soluble starches, they add 2 per cent. of the sulphuric ester of a mixture of octyl, decyl, dodecyl, tetradecyl and cetyl alcohols, whilst for dextrins the addition of 2 per cent. of the sodium salt of dodecylmercaptoacetic acid is recommended.

Such sulphated or sulphonated compounds, whilst overcoming one difficulty tend to introduce another and this is the production of foam. Adhesives may, and do, foam on occasions due to the presence of certain compounds, even when a wetting agent has not been added. Foam formation is controllable by the addition of octyl or cetyl alcohols.

Albumin derivatives of a salt-like character serve, according to the Sichel Komm-Gesellschaft and Stern,⁸⁶ to increase the spreading power and elasticity of starch adhesives when employed in amounts up to 10 per cent., calculated on the base of the starch used, e.g. the product obtained by the degradation of casein with hydrochloric acid may be used. In another patent of Stern's,⁸⁸ the paste obtained by the treatment of starch with sodium silicate is mixed with wetting agents, lecithin, or soaps, to improve the working properties; and the addition of 6 per cent. of naphthene soap has a favourable influence on the keeping properties of starch pastes according to the patent of Mahler and Supf,⁸⁹ who consider it superior in this respect to the fatty-acid or resin-acid soaps, for example, the ammonium resinate or rosin used by Grosvenor.⁹⁷

Herth⁹⁰ obtains an increase in adhesive properties and an increased gloss in textile dressings by forming a colloidal dispersion of inorganic materials *in situ* from reagents which give a precipitate by double decomposition. As an example, 10 per cent. soda ash and alum is added to a corn-starch paste.

The addition to pastes of solvents for grease and waxes in order to obtain adhesives for waxed papers is practised by a number of firms; thus the Sichel Komm-Gesellschaft⁹¹ adds toluene, xylene and similar solvents to the starch pastes, and after forming the emulsions find they are stable and of value for the pasting of waxed papers (*v.i.*).

Schluter⁹² adds decomposed grain flour to his starch before forming the paste, and it will be seen later that in one of the processes for manufacturing textile sizes it is customary to allow a flour suspension to ferment for some time before making the size, the claim being that a better adhesive action is obtained. A further point of interest is that an adhesive of good standing is made by the controlled fermentation of gluten, as mentioned

in the section on by-products. Another addition to starch in the preparation of an alkali starch adhesive is that made by Kreismann,⁹³ who incorporates a certain amount of potato pulp in the mixture.

The addition of borates to starch preparations has already been mentioned, but we may note here that the addition of certain borates to starch preparations increases their stability and smooth-working properties. If an alkali starch paste is made by, e.g. slurring 72 kg. potato starch in 140-150 litres of water and running into this 15 kg. of 30 per cent. caustic lye with constant stirring and heating; then on treating this paste with 120 kg. barium chloride in about 18 litres of water the barium starch is precipitated and can be filtered off. The product is an insoluble powder and can be kept in the dry state in admixture with alkali salts, such as borax. When the mixture of barium starch and borax is added to water the inorganic constituents react to give an adhesive paste.⁹⁴ Sodium sulphate can be used in place of the borax to effect the decomposition, and instead of the barium starch the calcium, aluminium, zinc, and magnesium complexes may be used.

A further modification⁹⁵ of the above process is to employ, for the decomposition, soluble metal salts other than those of the alkalis, e.g. calcium, aluminium, iron or copper salts, and these may be added at the time of preparing the alkaline-earth starch. It will be seen that many alternatives are possible in this process; the adhesives obtained vary from glue-like adhesives to smooth pastes, depending upon the metals used and the order of use.

The addition of alum, glycerine, and other hydroxy-compounds of a hygroscopic nature has already been discussed (see p. 155). For compounds used as antiseptic agents and preservative see Chap. 15. We may now pass on to the consideration of dextrin adhesives.

Dextrin Adhesives.—A great many dextrin adhesives are in everyday use and can be formulated to give smooth pastes having little tackiness when first applied, but which after a slight exposure to air give good adhesion when pressed into contact with another surface, for example, photographic mounting pastes or poster pastes. Dextrin glues can also be made which have great tackiness, like the 'pick-up' gums used in labelling or sealing of cartons or packages.

To give body to a dextrin adhesive a white dextrin may be used as the base, and the solid-content and tackiness increased by the addition of dextrans which have been converted much further. For example, if a hand-sealing adhesive for cartons or

paper is to be used, the tackiness of the paste need not be great, as the thin layer of adhesive is exposed to the air for an appreciable time before the joint is made. This condition is very different from that in which the adhesive is spread on by a machine and the joint made in a fraction of a second. In the second instance, tackiness is essential in order to hold the joint firmly together during the rapid progress through the machine.

A typical formula for a hand-sealing adhesive is as follows: A maize starch is converted by the action of malt extract until the iodine test gives a slightly reddish-blue colour and the sugar-content is 5 per cent. This material can be dried round hot rollers and stored for further use. The dried material is soaked overnight in twice its weight of water and then 10 per cent. of a medium-cooking white dextrin is added, and the temperature raised to 80° C. Five per cent. of borax is dissolved in a little water and added to the mass, followed by 2.5 per cent. of caustic soda and a small amount of phenol to act as a preservative.

As an instance of the type of formula used to obtain an adhesive for sealing wrappers by means of a machine the following formula may be noted. Fifty parts of water are brought to boiling-point and 40 parts of a well-converted yellow potato dextrin dissolved in it, after which 4 pts. of borax are added, and when this has dissolved 2 pts. of caustic soda, 0.1 pt. phenol and 0.05 pt. turkey-red oil are added in that order. It will be noticed that in this formula the tackiness has been increased by using a well-converted dextrin, and that the water-content has been decreased from that used in the hand-sealing formula, being approximately 51 per cent. as opposed to the 57 per cent. in the previous instance.

Cardboard used to make tubes, etc., is more absorbent than the paper employed for wrappers, so that in an adhesive to be used, e.g. in making spiral tubes, the water-content has to be still further decreased in order to obtain a thicker gum which will not penetrate into the cardboard and thus be lost for the purpose of joining the two surfaces. For this type of work a very sticky gum is required, and the dextrin mentioned in the precious paragraph may be employed. The water-content in this case is reduced to about 48 per cent., thus limiting penetration. The deep colour of the adhesive is no drawback for this type of work, as it is practically the same as that of the cardboard itself.

The plant for the manufacture of dextrin adhesives is generally simple in design, and may be either a jacketed pan provided with a stirrer, or a vat heated by means of live steam passing into the glue itself. The latter type is very efficient, and care should be taken before starting manufacture to put at various heights

graduation marks for indicating the weight of liquid contained in the vat, and then to pass in live steam until the temperature rises to $98-100^{\circ}\text{C}$. The increase in the amount of water from condensation of steam should be carefully noted and due allowance made for this factor in any mixings. The stirrers should be preferably of the gate type, revolving in opposite directions, geared to give 10, 20 and 40 revs. p.m. at will, depending on the size of the vat, as the peripheral speed will of course depend on this. The vats themselves should be preferably of wood, or of enamelled or lead-lined iron in order that discoloration of the light-coloured adhesives made in it may be minimised. The mixers should empty by gravity—for viscous pastes through a gate valve, and thinner pastes through a large cock fitted with a straining cloth. The lid of the vat should fit well and be lined preferably with copper sheet, except for enzyme conversions.

Borax and caustic soda are often added to dextrin solutions, and it is essential that the borax should always be added first and allowed to dissolve before the addition of caustic soda. If these compounds are added in the reverse order the glue becomes 'burnt,' i.e. loses most of its adhesive characteristics and turns a very deep brown colour. The borax buffers the action of the caustic soda and is generally added to the extent of twice the weight of the alkali, whilst the total amount of inorganic matter often amounts to 15 per cent. on the weight of dry material present.

When a standard set of dextrans has been acquired from a reputable maker, further deliveries of any dextrin should be compared against the standard for viscosity in solution, colour, sugar-content, and 'set-back'. As explained on page 108, 'set back' is the term used to denote the stability of the solution, or the tendency of the solution to go cloudy or thicken on standing.

Sodium perborate¹⁰⁵ is often added to obtain a bleaching effect, and at the same time the amount of borax produced by its decomposition must be allowed for in the formula when borax and caustic soda are to be added. The treatment of glues with this agent is carried out by adding a cold solution to the glue at a temperature of less than 35°C . after all the other ingredients have been added.

It should be remembered that bleaching agents, such as sodium persulphate and especially hydrogen peroxide, cause a marked decrease in the viscosity of dextrin solutions. The same effect is obtained when formaldehyde is added to the hot mix (see, however, p. 155), but the use of sodium perborate does not show this effect so much, as the borax formed by the action tends to increase the

viscosity and so rectify any drop in this value that may have occurred.

The addition of calcium chloride to a dextrin adhesive imparts an oily or 'lardy' appearance to pastes made from the mixture; it is one of the agents employed to give a slow-drying glue, glycerine being another. The solution containing calcium chloride and dextrin is often employed in adhesives for highly calendered papers, which are somewhat slow in wetting out, but the use of this agent is not entirely satisfactory for this purpose as sometimes there is a tendency for a discolouring stain to appear around the joint.

The sodium bisulphite which is added to dextrin adhesives sometimes acts as a bleaching and preservative agent, but its use tends to make the adhesive work badly on machines, owing to a strong tendency to ropiness. The same phenomenon is observed in the presence of salicylic acid, although, as already stated, this substance cannot be used as a preservative if the adhesive is liable to come into contact with iron, owing to the intense discoloration that follows contamination with iron salts.

Certain dextrans are supplied as powders containing all the ingredients necessary to make the adhesive, and all that is necessary is the addition of water. Some of these are called arable gums or envelope gums and are generally formulated on a fairly well-converted tapioca-dextrin base. They may contain up to 2 per cent. sodium bisulphite, of additions of borax and soda ash. On solution in water they yield yellow or brown, syrupy solutions which have excellent adhesive properties.

By careful processing, dextrin glues may be obtained containing gelatine, and such adhesives may be employed for joining cigarette papers that are used by those who prefer to make their own cigarettes. Pectin glue is another kind that can be used in conjunction with dextrin for this purpose.

For purposes in which the glue is to come into contact with the tongue, such as glues for envelopes or for stamps, a straight tapioca or maize dextrin may be employed; they have little taste or smell, whereas potato dextrin has a decided taste and an unpleasant smell.

For sticking waxed surfaces, several makers have evolved dextrin adhesives containing a solvent, like trichlorethylene, emulsified in them, but so far these mixtures have had no really outstanding success, whilst their odour constitutes a drawback for many purposes. Another problem confronting the adhesive maker is that of labelling tins, and the above type of adhesive has been used for this purpose. When the tins leave the factory

where they are made the surface is covered with a very thin film of palm oil or a fat, which is applied at one stage during manufacture. The thin film of grease prevents the adhesive from wetting the metal, and although adhesion between the metal and label is apparently good when the joint is first made, on drying the label peels off or is very easily removed. Some makers claim to have overcome this defect by the addition of wetting agents to the adhesive, but for some time now many makers have used a base other than dextrin for this type of work; in some cases the difficulty had been side-tracked by using a label which extends right round the tin and is gummed to itself on the small overlap left for the purpose. Most of the agents employed to pierce the film of grease generally cause rusting of the tin in time; caustic soda and nitric acid are old offenders in this respect and have therefore fallen into disrepute.

The type of dextrin known as crystal gum forms an excellent basis for adhesives to be used for delicate work. In some classes of work, such as lining boxes with coloured paper, the reaction to acid or alkali of the colour used on the paper has to be considered, some dyestuffs giving a change of colour in contact with acid, others with alkali. Crystal gum may be used for this kind of work, as it is generally neutral in reaction, free from starch, contains very little sugar, and very rarely contains chlorine or sulphur dioxide, both of which are very bad when present in adhesives used for colour work.

Crystal gum is generally made from potato starch, and although it is somewhat more expensive than ordinary dextrin, it is cheaper than other adhesives with similar properties and is very effective. It is sometimes used to make the wood filler in cabinet-making or in decorative work. It is used in conjunction with a filler, generally of the pigment or inorganic type. Barytes, china clay, kaolin or zinc oxide can be used where a white compound is required, but where a coloured filler is needed an ordinary dextrin is employed, as its colour is masked by the pigment. The following is an example of the type of formula used in this work: 2 lb. crystal gum are dissolved in 3-4 lb. hot water, and 5 lb. barytes and 2 lb. china clay are well mixed into the solution. Several ounces of driers are dissolved in 2 lb. boiled linseed oil and added to the hot crystal-gum suspension of the fillers. The resulting emulsion is then diluted to any required consistency with water. Synthetic resins are being used more and more, especially in the manufacture of moulded caps for bottles or jars used in the cosmetic and pharmaceutical industries. Many of these caps are lined with cork and are required to have labels affixed to them.

A composition for affixing such cork linings may be made as follows : 35 lb. of crystal gum are mixed with 45 lb. of gypsum, and another mixture made containing 6 lb. powdered fish glue, 10 lb. casein and 3 lb. soda ash or borax. When required for use the crystal-gum mixture is added to water, followed by the second mixture.

One adhesive is made by mixing 2 lb. of very finely powdered casein with 1 lb. crystal gum containing 1 per cent. hydrated lime or borax. This mixture is used as a fixative for dentures ; it is tasteless, odourless, and resistant to saliva and liquids in general. The adhesive properties remain for some time, as the alkali present serves two purposes : it assists the casein to dissolve and retards the rate of hydrolysis of the crystal gum, which already has a slower rate of hydrolysis than the ordinary dextrins.

Mention should be made here of the importance of using dextrins having a low dextrose-content for the manufacture of adhesives. Dextrins produced by the roasting method contain a lower proportion of sugar than dextrins produced in other ways, as we have seen in Part I, Chapter 6, and the dextrins mentioned in the preceding formulæ come into this category. Dextrose is more hygroscopic than maltose, which is the sugar formed in the enzyme process. The content of sugar in a dextrin to be used in making an adhesive should be around 2-3 per cent. for yellow dextrins and 4-7 per cent. for white dextrins, including those made by the wet method using enzymes. The reaction in the last method is generally stopped at a point where the iodine test gives a purplish-blue coloration, and it is found that the sugar-content at this stage varies, according to the starch used, from 5-7 per cent.

A dextrin containing an excessive amount of dextrose gives adhesives showing the phenomenon of 'crystallisation,' i.e. of drying rapidly on the surface ; the internal strains set up in this surface film during drying are sufficient to cause it to fly apart and many minute cracks to appear. When a satisfactory source of supply of dextrin has been found it is therefore as well to get all supplies from this source in order to ensure uniformity of deliveries, and to check this by chemical and physical tests on every new delivery.

As explained earlier in this section, the elasticity of the film is an important point, but for high-speed work on automatic machines it is not advisable to add such agents as glycerine, ethylene glycol, etc., to attain this end, as these agents, being hygroscopic, tend to absorb moisture in humid atmospheres and give rise to trouble on the machines. Ammonium sulpho-ricinoleate may be added

in place of these compounds for this type of work and does not suffer from the above defect; further, owing to its wetting properties, the adhesion is improved. Glycerine, etc., and glucose may, however, be used for some types of paper work and give the film of adhesive an enhanced brightness and plasticity.

If two surfaces of low permeability are to be joined, one of which is delicate in construction, i.e. metallised labels on perfume bottles, the adhesive should contain as little moisture as possible and, as previously mentioned in regard to adhesives for coloured papers, be neutral. A straight dextrin adhesive containing approximately 60 per cent. solid matter, about 1.6 per cent. formaldehyde, and a wetting agent should, after careful neutralisation with caustic soda, be found to give good results. A fairly soluble yellow dextrin will, of course, be employed in such mixtures in order to obtain a high solid-content with maximum workability.

The use of wetting agents has been mentioned several times and described for starch pastes; they may also be used for dextrin pastes. Varnished or highly calendered papers, and some metallic surfaces, are not easily wetted by straight dextrin-water solutions, but the presence of alkali in the 'mix' besides ensuring stability often improves the adhesion by assisting the adhesive to wet the surface. Alkali also tends slightly to erode some surfaces and thus gives the adhesive a chance to 'key' itself in. The propensity of alkalis to cause further corrosion after their first initial attack on the surface should be carefully watched, and also the likelihood of the gum being used for fugitive-coloured surfaces. Many wetting agents are neutral in reaction and very efficient in use; they may be employed not only for allowing a difficultly wetted surface to be joined, but also to assist in the wetting of a dried gummed surface, such as labels or envelopes. The addition of glycerine assists the latter operation, but such labels, etc., are liable to stick together in a humid atmosphere, whereas the presence of a small but effective amount of wetting agent inhibits this action but readily allows the label, etc., to be moistened by the mouth or moistening pad.

A point to be remembered in the formulation of an adhesive for gummed labels and papers is that a low-priced adhesive may be just as effective as a higher-priced one that has been made from lighter coloured, and therefore probably more expensive, materials. The film given by the lighter-coloured adhesive appears thinner than a layer of the darker adhesive of the same thickness, and prospective purchasers of the paper may gain the impression that the darker adhesive has been more freely applied. Unless

a light colour is actually demanded, therefore, it is preferable not to bleach the adhesive or to use expensive light coloured materials in the formula.

The increase in viscosity imparted by certain additions to adhesives has been mentioned above, and it is sometimes necessary that the viscosity of dextrin solutions should be increased or decreased in order to suit certain working conditions. If very porous paper or other surfaces are to be joined, the viscosity of the adhesive should be such that too much of the adhesive is not absorbed and so lost for joint formation, and this effect may be brought about by the inclusion of a certain amount of a fairly good grade gelatine in the mixture. To decrease the viscosity and allow a higher percentage of dextrin to be employed, the dextrin solution may be treated with formaldehyde. The amount of formaldehyde used may vary from 2.5 per cent., and even up to 30 per cent. in some cases, and the solution heated to 80° C. The colour of the solution is not darkened, nor are any other desirable characteristics of the film destroyed, in fact, a dextrin treated in such a way gives more lustrous and more easily-wetted films than a similar untreated dextrin. It should also be noted that many of the agents used to decolorise dextrin solutions tend to lower the viscosity, and this seems more apparent with the oxidising agents used for this work than with the reducing agents, hydrogen peroxide in particular markedly lowers the viscosity. It is interesting to recall that bleaching with oxidising agents is much more effective and lasting than bleaching with reducing agents, thus illustrating the more vigorous character of the former.

An *ageing test for envelope adhesives* is given by J. R. Adams¹¹⁰ and may be of interest. This worker encloses 50 envelopes in a small air-tight tin box which is maintained at 65° C. for 72 hours. The test is claimed to give the same amount of discoloration in the adhesive as 10 months' natural ageing in a semi-tropical climate without changing the colour of the paper to a noticeable degree. Interruption of the test for only a few minutes, e.g. by opening the box to remove a few samples, delays the development of the maximum discoloration for 24 hours. A loose-fitting lid on the box delays the appearance of the maximum discoloration for a longer period than this. The number of envelopes in the box is immaterial. Those papers sized with glue are most susceptible to discoloration, while other classes of paper are practically unaffected.

Enough has been said to illustrate the principles of adhesive-making with dextrins and to give some idea of the many possible

formulae that are available, only a very few of which have been quoted above.

REFERENCES

1. J. A. RADLEY, *Manuf. Chemist*, 1934, May.
2. J. W. MCBAIN and W. B. LEE, *Third and Final Report, Adhesive Research Committee*, H.M. Stationery Office, London, 1932, 66.
3. J. W. MCBAIN and D. G. HOPKINS, *J. Phys. Chem.*, 1925, **29**, 188.
4. MÉRIMÉE, *Bull. Soc. d'encouragement pour l'ind. nat.*, 1827, 118.
5. MARSDEN, U.S.P. 376,445, 1888.
6. J. KANTOROWITZ, E.P. 5844, 1896.
7. — E.P., 10,216, 1910.
8. — D.R.P. 157,896, 1903 ; U.S.P. 785,216, 1905.
9. — D.R.P. 158,861, 1903.
10. J. KANTOROWITZ, D.R.P. 160,259, 1905.
11. LEONHARDT, G.P. 408,523.
12. PERKINS, D.R.P. 282,699, 1911 ; U.S.P. 1,020,655, 1912.
13. — U.S.P. 1,020,656, 1912 ; 1,078,691, 1913 ; 1,078,692, 1913 ; 1,251,275, 1917.
14. GROSVENOR, U.S.P. 1,200,488, 1916.
15. GRÖNINGER, G.P. 302,832.
16. SUPF, G.P. 351,370.
17. PFEIFFER and SCHWANDER, G.P. 432,961.
18. H. BECHHOLD, G.P. 564,302, 1936.
19. O. MEYER, G.P. 447,727 ; E.P. 286,377, 1926 ; U.S.P. 1,773,056, 1930.
20. F. RIETHOF, Austrian P. 128,641 and 112,647, 1928.
21. SÄCHSISCHE KLEBSTOFFWERKE, G.P. 474,602, 1924.
22. HENKEL ET CIE, G.P. 582,679, 1926.
23. L. WEISS, U.S.P. 1,474,129, 1923.
24. A. SINGER, E.P. 188,344, 1922.
25. MAHLER and SUPF, G.P. 508,160.
26. HENKEL ET CIE, G.P. 508,786.
27. — G.P. 478,538.
28. — G.P. 479,143.
29. PFEIFFER and SCHWANDER, G.P. 527,140.
30. LEONHARDT, G.P. 412,125.
31. MAHLER and SUPF, G.P. 364,314.
32. SICHEL and STERN, G.P. 349,280 ; G.P. 372,794.
33. RUNGE, G.P. 381,516.
34. SICHEL and STERN, G.P. 389,748, 1920.
35. — G.P. 415,092, 1920.
36. KLEBSTOFFWERKE COLLODIN, G.P. 414,979, 1920.
37. HAAKE, G.P. 547,421, 1926.
38. SOC. ANON. DES RECRIS FRANÇAISES, G.P. 406,540, 1923.
39. E. STERN, *Zeit. angew. Chem.*, 1928, **41**, 88 ; G.P. 519,300, 1924.
40. — E.P. 272,274, 1926.
41. — U.S.P. 1,661,201.
42. HEIM, G.P. 453,501, 1924.
43. J. SELLARS, E.P. 2810, 1865.
44. A. SCHUHMAN, E.P. 5460, 1887.
45. W. P. THOMPSON, E.P. 7272, 1891.
46. — E.P. 21,973, 1906.
47. F. A. V. KLOPPER, G.P. 528,109, 1930.
48. H. H. LAKE, E.P. 5617, 1893.
49. C. B. DURYEA, U.S.P. 675,822, 1901 ; U.S.P. 696,949, 1902.
50. BERGQUIST, U.S.P. 1,287,841, 1918.
51. P. MURPHY, U.S.P. 568,265, 1896.
52. BROWNING and BARLOW, U.S.P. 773,469, 1904.

53. B. HELFERICH, A. STÄRKER, and O. PETERS, *Ann.*, 1930, **482**, 183.
54. K. FREDENHAGEN and B. HELFERICH, U.S.P. 1,883,676, 1932.
55. I. G. FARBENIND., G.P. 560,535.
56. H. SCHENBACH, G.P. 554,699; G.P. 566,515.
57. R. W. G. STUTZKE, U.S.P. 1,320,719, 1919.
58. H. COURTONNE, *Compt. rend.*, 1920, **171**, 1168.
59. MÖLLER-HOLTKAMP, U.S.P. 793,600, 1905.
60. J. ALEXANDER, U.S.P. 1,337,382, 1920.
61. REYCHLER, *Bull. Soc. chim. Belg.*, 1920, **29**, 118.
62. L. EYNON and J. H. LANE, *Starch*, W. Heffer & Sons, Ltd. Cambridge 1928.
63. D. R. NANJI and R. G. L. BEAZELEY, *J. Soc. Chem. Ind.*, 1926, **45**, 215T.
64. ARABOL MAN. CO., F.P. 394,167, 1908.
65. NEUSTADT, G.P. 392,660, 1921.
66. WATTECAMPS, G.P. 444,576, 1925.
67. KÜHL and SOLTAN, G.P. 522,555, 1928.
68. STEIN, G.P. 390,478, 1919.
69. J. KANTOROWITZ, U.S.P. 1,677,348, 1928.
70. MAHLER and SUPF, G.P., 371,407, 1918.
71. — G.P. 389,023, 1921.
72. E. MEUSEL, *Jahresb. Chem.*, 1886, 2099.
73. HENKEL ET CIE, E.P. 359, 756.
74. — E. P. 276,340.
75. — G.P. 308,616 and 406,820.
76. — E.P. 244,708, 1924.
77. R. MAUCH, *Archiv. Pharm.*, 1902, **240**, 166.
78. E. SCHAEER, *Pharm. Centralhalle*, 1896, **37**, 540.
79. HENKEL ET CIE, G.P. 563,272.
80. E. F. HOPPLER and J. W. HAAKE, E.P. 346,224, 1930.
81. JAGENBERG-WERKE A.G., E.P. 441,658; F.P. 783,963, 20/7/1935.
82. CORN PROD. REF. CO., U.S.P. 2,165,834.
83. HOLZHYDROLYSE A.G., G.P. 605,016.
84. W. SCHRAUTH, U.S.P. 2,051,184; 18/8/1936.
85. HENKEL ET CIE, E.P. 432,486, 1934.
86. SICHEL KOMM-GES., G.P. 359,519.
87. HENKEL ET CIE, G.P. 554,988.
88. E. STERN, E.P. 447,810.
89. MAHLER and SUPF, G.P. 556,448.
90. HERTH, G.P. 395,647.
91. SICHEL KOMM-GES., G.P. 455,014, 9/10/1925.
92. SCHLUTER, G.P. 572,052.
93. KREISMANN, U.S.P. 1,490,330, 1924.
94. E. STERN, G.P. 519,300.
95. — G.P. 542,581.
96. W. M. GROSVENOR, U.S.P. 1,378,105, 1921.
97. — U.S.P. 1,311,965, 1919.
98. R. DULAC and J. L. ROSENBAUM, *Industrial Cold Adhesives*, Griffin & Co., London, 1937.
99. G. E. CORSON, U.S.P. 1,977,514, 1934.
100. PERKINS, E.P. 427,880, 1935.
101. E. H. HARVEY, U.S.P. 1,790,346, 1931.
102. W. SCHULZE and C. BEYER, E.P. 466,287, 1937.
103. — *Biochem. Zeit.*, 1938, **292**, 141.
104. M. SAMEC, *Kolloidchem. Beih.*, 1912, **4**, 132; 1913, **5**, 141.
105. L. FACKLER, U.S.P. 1,618,150, 1927.
106. F. CAMPS-CAMPINS, *Paper Trade J.*, 1940, **110**, 120.
107. H. F. BAUER, U.S.P. 2,183,736, 1939.
108. R. L. DATTA, S. C. SEN and N. N. BOSE, *Manuf. Chem.*, 1940, **11**, 197.
109. N. A. SPASSKII, *Poligraf. Proizvodstvo*, 1938, No. 1, 33; via *Chem. Zentr.* 1938, II, 2547.

110. J. R. ADAMS, *Techn. Assoc. Papers*, 1939, **22**, 174; *Paper Trade J.*, 1939, **109**, No. 9, 31.
111. V. I. NAZAROV, *J. Applied Chem.*, U.R.S.S., 1939, **12**, 1745.
112. L. EYNON and J. H. LANE, *Starch*, W. Heffer & Sons, Ltd., Cambridge, 1928.
113. L. T. SMITH and R. M. HAMILTON, *Chem. Eng. News*, 1944, **22**, No. 17, 1482.
114. C. R. SINGLETERRY, *Paper Trade J.*, 1941, **113**, No. 8, 37.
115. A. KIRKPATRICK, an unpublished paper read before Soc. of Rheology, Pittsburgh, 28/12/1938 (via Ref. 113).
116. J. W. MCBAIN, *Nature*, 1927, **120**, 362.
117. — and G. P. DAVIES, *J. Amer. Chem. Soc.*, 1927, **49**, 2230.
118. — and D. G. HOPKINS, *J. Phys. Chem.*, 1925, **29**, 182.
119. — — — *ibid.*, 1926, **30**, 114.
120. — and W. B. LEE, *Ind. Eng. Chem.*, 1927, **19**, 1005.
121. — — — *J. Phys. Chem.*, 1927, **31**, 1674.
122. — — — *ibid.*, 1928, **32**, 1178.
123. — — — *J. Soc. Chem. Ind.*, 1927, **46**, 321.
124. W. D. HARKINS, *Colloidal Symposium*, 1925, **3**, 48.
125. —, F. E. BROWN and E. C. DAVIES, *J. Amer. Chem. Soc.*, 1917, **39**, 354.
126. —, G. L. CLARK, and L. E. ROBERTS, *ibid.*, 1920, **42**, 700.
127. — and W. W. EWING, *ibid.*, 1920, **42**, 2539.
128. — and E. H. GRAFTON, *ibid.*, 1920, **42**, 2534.
129. — and A. FELDMAN, *ibid.*, 1922, **44**, 2665.
130. N. A. DE BRUYNE, *Aircraft Eng.*, 1939, **18**, 51.
131. E. E. HALLS, *Plastics*, 1941, **5**, 123.
132. J. J. BIKERMAN, *J. Soc. Chem. Ind.*, 1941, **60**, 23.
133. J. ALEXANDER, *Colloid Chemistry*, Vol. I, Chap. I, Chemical Catalogue Co., N.Y., 1926.
134. H. H. HOUTY, *Paper Trade J.*, 1941, **113**, No. 6, 32.

ADDITIONAL REFERENCES

- F. HOLT, *Paper Ind.*, 1935, **17**, 482, 760. (General.)
- C. BECHER, *Gel. Leim. Klebst.*, 1934, **2**, 113. (General.)
- *ibid.*, 1935, **3**, 54, 87, and 163. (General.)
- E. RINGINBACH, E.P. 465,301, 1937. (Starch pastes.)
- DUEROU, *Recherches et inventions*, 1935, **16**, 254. (General.)
- C. F. MASON, *Chem. Industries*, 1936, **39**, 171. (General.)
- HENKEL ET CIE, F.P. 816,967, 1937. Equivalent to E.P. 479,316. (Salts of sulphonic-acid derivatives of starch ethers.)
- F.P. 808,699. Equivalent to E.P. 478,299. (Salts of cellulose-ether carboxylic acids mixed with starch.)
- DEUTSCHE HYDRIERWERKE A.G., G.P. 653,186, 1937. (Aliphatic sulphuric esters used in starch pastes.)
- H. T. MAYER, *Gel. Leim. Klebst.*, 1938, **6**, 107. (Potato-starch adhesives of the neutral type.)
- P. KREISMANN, U.S.P. 1,667,073, 1928. (Potato starch, clay and aqueous alkali heated until semi-fluid glue obtained.)
- H. V. DUNHAM, U.S.P. 1,551,472, 1925. (Glue. Heats starch with water and alkali-saccharate.)
- P. D. COPPOCK, U.S.P. 2,181,782, 1939. (Dextrin rendered non-lumping in water by heating between hot plates under pressure.)
- I. F. WALSH and W. L. MORGAN, U.S.P. 2,170,271, 1939. (Thin-boiling starch by treatment with an amide-hydrochloride.)
- U.S.P. 2,170,272, 1939. (Acid salts of amides or amino acids claimed to thin starch.)
- F. OHL, *Kunstdünger u. Leim*, 1934, **31**, 207; 1938, **35**, 309. (Practical suggestions on adhesives for use in cardboard industry.)

- M. M. BARNETT, *Polygraph Ind. (U.S.S.R.)*, 1937, No. 9, 29; *Chem. Zentr.*, 1938, I, 3294. (Alkali-starch adhesives described.)
- W. R. LANGE, U.S.P. 2,633,640, 1947. (Hydrolysed maize starch mixed with carboxylic acids and borax to give a glue.)
- E. R. HEDSON and G. E. MACH, U.S.P. 2,192,585, 1949. (Envelope gum, Dextrin and urea.)
- M. BARNETT, U.S.P. 2,386,444, 1946. (J. B. KEMP's reaction used to obtain glues from starch.)
- F. B. DEXTER and J. R. ALLEN, U.S.P. 2,392,242, 1949. (Envelope glue from dextrin, water and dioxane.)
- R. DATE and J. F. WATSON, U.S.P. 2,391,558, (Destarching maize starch containing gluten.)
- R. M. HIGSON and G. F. BRIDGEMAN, *Ind. Eng. Chem.*, 1942, **34**, 959. (Waxy starch of maize as a possible substitute for tapioca starch in adhesives discussed.)
- L. C. WOODRUM and F. L. GARDNER, U.S.P. 2,489,170, 24/11/1949. (Asphalt having AFTM D-5 penetration of 250-50 added to starch-urea-formaldehyde resin adhesives to reduce costs without impairing quality.)
- R. W. BRIDGEMAN, U.S.P. 2,487,445, 5/11/1949. (Raw starch, polyvinyl alcohol and clay mixture heated in water to give adhesive. Remarkable water resistance claimed.)
- P. A. SUGAN, U.S.P. 2,473,486. (Adhesives by treating 25-50 per cent starch pastes with diastase and progressively raising the temperature to the boil as the viscosity falls, cooling, adding more malt diastase, holding and then boiling.)
- H. S. PATER and R. WARD, U.S.P. 2,424,994, 26/2/48; Appl. 26,142. (Adhesives from sweet potatoes by steaming with SO_2 and petrol vapour, pressing out water, drying, grinding, sieving, then treating with NaCl or CaCl_2 .)
- J. P. KILBROOK, *Paper Trade J.*, 1943, **117**, 1474, 1475. (Discusses production of weatherproof, laminated fibreboard adhesives, including urea-formaldehyde resins, starch and starch/asphalt combinations.)
- A. HERMAN and F. M. BROWDER, *Proc. Amer. Soc. Testing Materials*, 1942, **42**, 956. (Testing the value of starch pastes as adhesives for bottle labelling and paper packaging described.)
- ROMM and HASS CO., U.S.P. 2,459,399 and 2,462,419. (Partially hydrolysed starch mixed with soluble urea-formaldehyde reaction-product and heated.)
- H. F. BAUER, U.S.P. 2,215,846-7, U.S.P. 2,215,849, 24/9/1949. (Wheat starch conversion product mixed with urea, sodium acetate or other plasticising agent to give a remanishing gum.)
- LE PAGE'S INC., U.S.P. 2,462,364. (Adhesive from starch and dicarbamide.)
- C. BECKER, *Gel. Lebn. Abstr.*, 1942, **10**, 27. (Several tables of formulae of approx. composition for variety of starch adhesives.)
- L. E. KILBROOK, *Paper Trade J.*, 1943, **117**, 28 (9). (Reviews starch-urea-formaldehyde resin combinations as adhesives.)
- ROMM and HASS CO., U.S.P. 2,453,423, 5/9/49. (Stabilisation of starch pastes with urea- or thioure-formaldehyde compounds.)
- G. H. OSOSON and R. G. PETERSON, U.S.P. 2,441,303, 27/12/38; Appl. 36,1034. (Raw starch mixed with a partly condensed mixture of an aldehyde and a substance which will condense therewith, e.g. urea, diurea or phenol, an excess of aldehyde, zinc chloride and sulphate and protein colloid to give a waterproof adhesive.)
- S. V. GRADIN and J. L. THOMAS, U.S.P. 2,466,680, 21/2/49; Appl. 36,1034. (Starch/urea-formaldehyde resin mixtures as adhesives.)
- H. F. BAUER, J. V. BAUER, and D. M. HAYLEY, U.S.P. 2,396,937, 19/3/46; Appl. 4,10048. (Starch adhesives which swell but do not dissolve in fully de-aerated hot or cold water made by heating dry converted starch with aldehyde.)
- C. C. LINDEN and D. RYAN, U.S.P. 2,421,562, 16/9/47. (Improved cereal

starch adhesives by heating starch with water and salt of amphoteric metal or copper in the presence of NaOH and soap.)

R. L. DATTA and N. N. BOSE, *Mfg. Chemist*, 1945, **16**, 315, 322. (Alkaline starch adhesives discussed.)

E. MONTORSI, *Pittura e. Vernici*, 1946, **2**, 92. (Adhesives by oxidation of cassava starch in alkaline medium in presence of Marseilles soap.)

E. H. HILL and V. X. SLIWINSKI, *Paper Trade J.*, TAPPI, 1949, 297. (Water resistance of starch pastes is inversely proportional to degree of conversion. Resin/starch mixtures recommended for water-resistant work.)

CHAPTER 9

THE FOODSTUFFS INDUSTRY

THE chemistry of starch is of great interest to foodstuff manufacture, as it constitutes an excellent raw material which can be used when an inert, neutral, edible filler is required, where liquids such as soups, etc., are to be thickened, or where gels are required, as with blancmanges, custard powders, etc.¹ As starch constitutes one of the major components of flour, its behaviour is of particular interest to the baking trade, whilst its presence contributes to the character of potatoes, when these are cooked.

When starch is used for food preparations its properties which are of direct interest to the food manufacturer are colour, freedom from dirt and fibre, viscosity, body, and temperature range of swelling. The importance of a number of these points becomes obvious when it is realised that pure starch added to food influences the texture and consistency. Flavour is of minor importance although the various starches have characteristic flavours but these are largely masked in the final dish. The question of availability and price may also have some influence on a manufacturer's choice of starch, but as a large amount of the pure starch used in the food industry is sold in small packets to the housewife her preference is also of great importance.

Many cooks use starch for such diverse purposes as thickening gravies and soups to making sweet puddings. For such purposes prepared starch in packet form is often in direct competition with the wheat flour found in nearly every British and American and many Continental households whilst in the latter potato starch or, more often, potato flour is in customary use. For such purposes wheat, rice, potato and maize starches are often interchangeable with each other and with wheat flour which contains between 70 to 80 per cent. starch.

The following chapter cannot assume to be more than a brief résumé of the immense amount of work done on starch in relation to foodstuffs, but the importance of the part played by starch in the properties of certain foodstuffs will readily be seen. Those interested in the chemistry of the potato should consult the paper by L. H. Lampitt and N. Goldenberg,⁶³ whilst the chemistry

of cereals has been fully and authoritatively dealt with by D. W. Kent-Jones and A. J. Amos.³⁶

The manufacture of glucose, maltose and alcohol has already been discussed.

Potato Products in the Food Industry.—In Germany there are several thousand potato-alcohol distilleries and a similar number of starch and glucose factories. Besides glucose and starch a large amount of potato meal or flour is produced and is used in home-made pastries and bread. Its manufacture on the Continent is carried out either in large central factories, with an output of 100 tons or more a day, or in small portable plants.

Potato flour enables potatoes to be kept in a form which eliminates the loss usually met through frost, decomposition, etc., whilst the bulk is very greatly reduced.

The starch-content of edible varieties is generally about 14-17 per cent., of which 1 per cent. or so is usually unrecoverable. Industrial varieties contain from 18 to 23 per cent.—occasionally 25 per cent.—but are not suitable for food purposes in normal time owing to their poor flesh colour and high fibre content.

To make potato flour the tubers are well washed, pulped and then steamed under about two atmospheres' pressure, air being blown through the hot pulp at the beginning of the steaming process to remove any volatile impurities from the pulp.⁶⁴ This procedure improves the smell and flavour and at the same time removes those impurities which tend to hydrolyse the starch to glucose. At the end of half an hour the material is discharged into a vessel containing water where the peel and heavy impurities sink to the bottom and the rest of the liquor is dried in a band or other type of dryer, or in the most modern plants a spray dryer is used.

Potato flour will keep for many years and contains 8-9 per cent. proteins, 0.2-0.5 per cent. fat, 80-82 per cent. carbohydrates and 2.0-2.5 per cent. ash.⁶⁵ In some cases the moisture-content is allowed to rise to some 18 per cent.⁶⁴

In the U.S.A. and Canada potato starch is blended with maize, tapioca or wheat to produce varieties of custard, blancmange and pie-filler powders. In cake mixtures, especially those of the waffle and sponge-cake type, a far superior product is said to be obtained by using up to 40 per cent. of potato flour to replace the wheat flour,⁶⁵ but a safer figure for shortbread, gingerbreads, cake and ordinary bread is probably 20 per cent. Some workers consider 50 per cent. can be added for bread-making, but the harsh flavour of the potato flour is accentuated. The consequent reduction in gluten is met by increasing the egg-content, although

not in the same proportion. Potato starch is also used in soup and gravy powders.

Moore and Partridge⁶⁶ record the use of boiled potatoes in bread-making to improve the whiteness of the bread. Contemporaneous usage in the U.S.A. calls for an addition of 10-20 per cent. of potato flour, with or without the addition of corn meal to reduce excess elasticity or 'dough tightness'. This practice permits the addition of greater amounts of water and the complete hydration of the gluten.⁶⁵ As an improver of crumb texture and colour the further claims have been made for potato flour that it has anti-staling properties and imparts a flavour that is valuable in the baking of brown, and especially rye breads. H. E. Cruz Monclova finds that good quality breads can be obtained when 20 per cent. of *cassava flour* is mixed with wheat flour, but more yeast than usual and potassium mono-hydrogen phosphate must also be included.

Importance of the Storage History of Potatoes.—According to J. Wright⁶⁷ and Barker⁶⁸ the sugar-content of potatoes may vary from 0.2-6.8 per cent. and is dependent on the storage temperature.

TABLE X

Sugar.	Observer, Ref. No.						Additional Data
	67.	78.	79.	91.	92.	93.	
	%	%	%	%	%	%	%
Reducing	0.91-1.99	—	0.72	0.05	0.17-0.35	0.3	—
Sucrose	0.27-0.34	0.04	0.67	0.14	0.51-0.6	0.2	0.1-0.26 ⁹⁴
Total	1.18-2.26	0.09-0.12	1.39	0.25	0.74-0.86	0.5 {	1.25-2.28 ⁹⁵ 0.26 ⁶⁸

When potatoes are stored the following reactions take place :—



Lowering of the temperature to below 4.5° C. leads to the formation of more sugar and at 0° C. 3 per cent. of sugar is the equilibrium concentration.⁶³ According to Barker⁶⁹ sugar formation can take place at temperature as low as 20° C., and other workers have also studied the low-temperature storage of potatoes. Wright⁶⁷ found an increase in both sucrose and reducing sugars on low-temperature storage, and Barker⁷⁰ considers that sucrose, or possibly the fructose half of the sucrose molecule in the labile

γ-fructose form, may be the respiratory substance. When the temperature is raised the sugar-content decreases⁷¹ and may possibly be used up in respiration. The starch-sugar balance is not only dependent on the temperature but may be influenced, according to Barker, by its previous temperature treatment. He has suggested⁶⁸ that during cold storage an irreversible accumulation of a 'depressant' occurs which is developed at high temperatures. This would explain why storage at low temperatures depresses the respiratory action in a manner which subsequent storage at high temperature fails to overcome.

Prior exposure to higher temperatures increases the sensitivity of the starch-sugar balance, whilst a process of acclimatisation to intermediate lower temperatures has the opposite effect.

Colour of Potato Chips.—When potatoes are baked or fried the sugars present are caramelised and the coloration of the products obviously depends on the quantity of sugar present.

F. G. Denny and N. C. Thornton⁷³ confirmed earlier work that storage of potatoes at 5° C., at which sprouting was inhibited, induced the formation of so much reducing sugar that the chips made from the potatoes were too dark. Storage at 10° C. or above gives rise to sprouting if stored too long at this temperature. The storage of potatoes to be used for chip-making is therefore of great importance. A content of 5 mg. of reducing sugar per ml. of juice (4 mg. per gm. of fresh potato) is the optimal concentration. The total content of sugar is no guide in selecting potatoes able to give the attractive golden-brown colour when fried, but with American varieties the reducing sugar-content is an extremely good guide. Whether this holds for English and other varieties remains to be seen.

Thus we see that the previous temperature history of potatoes is of great importance when they are to be used for making chips. On baking or frying less losses are encountered than with other methods of cooking potatoes.^{74, 75}

Cooking other than Frying.—Potatoes in their 'jackets' lose less than peeled potatoes when cooked,^{74-77, 100-106} whilst steaming is more preferable in this respect than boiling.⁷⁵⁻⁷⁷ If the potatoes are given a preliminary soaking in water or entered into cold water and brought to the boil, the losses are increased. In the case of boiled potatoes these losses are due to the leaching out of sugars, starch, nitrogenous compounds and mineral salts but the moisture-content is slightly increased.^{78, 79}

Many workers have found the vitamin-C content of potatoes to decrease on cooking in an amount dependent on the method used.

On cooking, the cells of the tuber separate, causing mechanical

disintegration, the starch is partially gelatinised, the pectins degraded, the cellulose becomes more digestible and the proteins coagulate. Sweetman⁸⁰ has discussed the physico-chemical changes taking place on cooking, and Personius and Sharp⁸¹ have followed certain of the changes taking place by means of tensile-strength determinations and find that no loss of strength occurs at 50° C., but above this there is a progressive loss which reaches a definite value for each temperature. As the weakening occurs prior to the gelatinisation of the starch this takes place independent of cell separation. These workers confirmed this conclusion by gelatinising the starch in the potatoes by immersion in 40 per cent. chloral hydrate, 2N sodium salicylate or ammonium thiocyanate followed by a treatment with a 0.5 per cent. solution of ammonium oxalate to soften the tissues. Only when the starch-gelatinising agent and the tissue-softening agent were used in succession was it possible to obtain a 'cooked appearance,' either agent alone being ineffective in producing this effect. They concluded that, on cooking, gelatinisation of the starch and a marked decrease in the cell adhesion of the tissues takes place.

The texture of the cooked potato appears to be governed by some other factor as the chemical cooking produced the same effect as normal cooking when 'mealy' or 'soggy' potatoes were used. Sweetman⁷⁵ found no positive correlation between mealiness and the starch-content of potatoes and, so far, the cause of mealiness has not been explained. That it is a function of the damage to the pectins present was suggested by Sweetman,⁷⁵ but Barmore⁸² obtained no correlation between pectin-content and mealiness in potatoes of equal starch-content.

Dumanski⁸³ found that the bound water increases from 0.567 gm. to 1.506 gm. per gm. dry solids on cooking, and it is possible that the resulting texture is dependent not only on the starch but also on the total, or bound, water of the partially gelatinised starch.

Rathsack⁷⁷ has introduced a Disintegration Index, Z, and a Texture Index, S, and found that Z is independent of, but S positively related to, the starch-content of the potatoes.

The Gelatinisation of Starch.—As stated above starch is insoluble in cold water, but when a suspension in cold water is poured into boiling water, or is itself boiled, the granules swell and, on cooling, forms a jelly when the concentration of starch present is high enough. Rice and maize starch both form 'short' opaque white gels if heated above 75° C., whilst translucent rather adhesive gels are formed from potato or tapioca starches if these are heated to about 70° C. with five to ten times their weight of water.

Professor Sybil Woodruff has examined and photographed gels made at different temperatures from starches used in the Food Industry, and her photographs constitute excellent permanent records of the differences in physical appearance that otherwise could not be described adequately. The outline of a gel turned out from a mould gave good indications of its character, although differences were noted in opacity, tenderness and freedom from stickiness. The addition of sucrose, such as is made in some sweetened starch puddings, was found to lower the gel-strength.

Chapman and Buchanan⁶² have studied the syneresis or slow separation of water from gels of maize, wheat, rice and potato starches and consider that neither the rate nor the time of heating the suspension affects the rigidity or the amount of syneresis in the resulting gels. The importance of this will not be overlooked by those interested in blancmange and custard powder manufacture.

When heating starch suspensions the opacity slowly decreases and at the temperature of gelatinisation it falls quickly to a minimum value which is not affected by heating for a longer time or at a higher temperature. Heating to this point, however, is insufficient to produce good gels since, as explained above, all the granules are not fully swollen. If the heating is continued to about 100° C. well-formed gels are formed from 5 per cent. suspensions of maize, rice and wheat starches, but potato, arrowroot and tapioca starches give soft or quite fluid gels. The rice gel is the most translucent and tender, the maize the firmest and whitest, while wheat starches give a gel of intermediate characteristics. Potato starch gels are ropy, transparent and stick to the mould, arrowroot gives a still more transparent and softer gel, whilst tapioca starch does not give a gel at the concentration used.

The results show that to obtain the maximum strength of the gel it must be heated well beyond the temperature at which the opacity suddenly decreases. In ordinary cooking, of course, temperatures of 90-100° C. are readily reached. With potatoes properly cooked internal temperatures of 100-104° C. have been recorded, but if the internal temperature reaches only 97° C. the potato is underdone. In biscuits and muffins a temperature of 100° C. is reached, but in these cases, however, it must be remembered that the granules cannot be completely swollen as the amount of water is very limited. If starch containing about 45 per cent. moisture is heated to 90-100° C. the granules swell but do not gelatinise and remain as discrete particles.

When starch is examined microscopically between crossed

Nicols prisms the granules appear strongly birefringent and the birefringency disappears when the granules gelatinise. Alsberg and C. P. Griffing² have examined breadcrumbs microscopically and found that although birefringent masses could be seen no individual birefringent granules could be detected. This is explained by Woodruff's observation³ that the temperature at which birefringency disappears, i.e. at which the granules are swollen, depends on the amount of water available.

The Effect of Various Factors on Gel-Strength of Starch Pastes.—In making custard or blancmange powders another point of interest is that different strengths may be obtained by the use of different batches of the same starch, as Woodruff⁴ has found that the ability of a starch to form a gel can vary according to the source of the starch. She found⁴ that gels of maize starch made from corn which has suffered from heavy frosts before it is completely mature do not leave the mould as cleanly as usual but that the ability to form a gel did not appear to be noticeably affected.

Another important factor is the effect of the purification processes during manufacture of the starch. It is customary to steep maize in water containing sulphur dioxide (see p. 46) to reduce bacterial and fungoidal growth, to increase the speed of softening and to give the final product a good colour. Starch separated without the use of sulphur dioxide, however, gives stronger gels than that made using the normal sulphur dioxide treatment.

With wheat starch an improvement in colour together with an improvement in baking properties is obtained by bleaching, which can be carried out in about five different ways. The bleaching process is very akin to the sulphur dioxide treatment of maize, but Woodruff (*vide supra*) found that such treatment has little or no effect on the gel-forming properties of the wheat flour. This is probably due to the fact that the gelling power and the viscosity of maize-starch pastes are more readily affected by the addition of chemicals or the pre-treatment of the starch than is the case with wheat starch.

The effect of freezing on starch pastes is interesting (see also Vol. I). and may hold some interest for food processers not only from the foodstuff point of view but also because they may be using starch pastes for adhesives in some part of the factory. By freezing and then thawing a starch paste the jelly-like structure is destroyed and a spongy mass results. With maize starch the water can be squeezed out readily by hand after which it will readily soak up water again without, however, giving the original

gel. From wheat starch the sponge formed retains the water more firmly than that from maize starch and is not so tough (Woodruff⁵). When allowed to dry it gives a very tough, horny mass differing very markedly from that obtained by drying maize-starch 'sponge'.

It is interesting to note that the appearance and properties of the gels changed to a much greater degree when the pastes were frozen at -2° to -3° C. than when frozen at a much lower temperature. In this connection it must be mentioned that bread-staling occurs much faster at -2° to -3° C. than at any other temperature. At the temperatures given by solid carbon dioxide or liquid air the rapid formation of small ice crystals and the lack of facilities for orientation of the starch molecules probably explains the lesser change which takes place on freezing at these low temperatures. After freezing to such low temperatures the pastes, on thawing, have a consistency very similar to a freshly gelatinised paste, and microscopical examination shows that it has a very 'short' or 'brittle' appearance, whereas paste frozen at -2° to -3° C. shows a ropy network. Woodruff has shown pastes frozen below this temperature gave the smooth form on thawing, but if this temperature is not reached then thawing produces the ropy form (see also Vol. I).

With starch from different varieties of maize it has been found that the gel-strength of the pastes varies over a wide range, the starch from white corns giving stronger gels than those from the yellow types. The viscosity differences between these pastes are not very pronounced, but if a pectin-jelly-strength tester be employed to measure the gel-strength of these pastes wide variations are encountered. Thus a test based on a gel-strength would appear to be more valuable to the food manufacturer than one based on the more usual viscosity test which does not show the effect of poor growing conditions or of frost on the growing corn which is reflected in the gel-strength of the starch made from such corn. Another point of interest is that rapidly raising the temperature to 95° C. gives a firmer gel than slowly heating to that temperature.

Uses of Starch in Various Foodstuff Preparations.—Maize, tapioca, and rice starches or flours have all been used in the manufacture of *custard powders*, *ice-cream powders*, *cake powders*, *blancmange powders*, etc. Other substances, such as sugar, essences, and colours, are also added to meet special requirements. The addition of essences and colour is generally made by first preparing a small master batch, which is carefully incorporated with the rest of the mixing. If the colour is added as a solution,

care must be taken to strain out any undissolved particles of dye-stuff before it is added to the starch, and to dry the coloured starch at a suitably low temperature so as to avoid gelatinisation of the starch and the formation of small lumps.

Tapioca pudding is a well-known dish in this country and America, being bought as a prepared, precooked product either as 'flake' or 'pearl'. The 'flake' variety is a granular quick cooking type whereas the 'pearl' variety which requires soaking for some hours before cooking or else a rather lengthy cooking process. The granular type is made by heating moist cassava or tapioca starch on iron plates with stirring which loosens the gelatinous starch from the heated plate so that it flakes off as tough sheets. These are dried and ground to the desired mesh size. Seed or pearl tapioca is made by rocking a layer of sieved starch on a hammock-like contrivance so that the starch particles adhere to each other and these aggregates build up to a more or less spherical shape by the motion of the hammock. The pearls are then sieved in order to grade them according to size ('bullet', 'medium' or 'seed'), cooked on a hot iron plate as for the flake products, regraded for size by sieving and dried ready for sale.

A more modern method is to extrude the moist tapioca starch through circular orifices in an iron plate, tumbling the pellets so obtained in a revolving steam heated jacket until vitreous in appearance.

The stoppage of supplies of tapioca products due to the Japanese occupation of the Dutch East Indies led, in America, to a revival of interest in the waxy varieties of maize, barley, rice and grain sorghums which have long been known to simulate the characteristics of cassava starch. American agronomists rapidly produced new sorghum hybrids in Kansas, Texas and Nebraska and a large acreage of Iowa was soon under waxy maize. The domestic source of these waxy starches has attained such importance in the brief time they have been introduced that America may not need to import cassava starch again, for such purposes. In the adhesive and textile fields also these starches are capable of replacing cassava starch so that price considerations will probably be the dominating factor as to whether the latter starch has lost the market in the United States. Prior to the 1939-45 war tapioca constituted from 11-14 per cent. of the total of starch consumed for food purposes in the U.S.A. Up to the present, however, no apparatus which is commercially successful appears to be in operation outside Java where native labour contributes much to the low cost of the product.

Blancmange type puddings and custards require the use of a

tarch which has a velvety and 'short' texture such as is shown by maize starch. The various points with regard to the physical behaviour of maize starch for these uses have been discussed above as also has the method of addition of the colours and essences. A typical recipe for a prepared pudding type is:— 25 lb. maize starch, 65-75 lb. sugar, 1 lb. salt, 3 oz. natural vanilla essence.

Starch has also been used as a carrier for organic peroxides in bleaching flour,⁸⁵ and as a filler in *improvers and bleaching agents* for use in dough.⁸⁶ E. V. McCollum and O. S. Rask⁸⁹ have introduced a so-called solid form of lactic acid for use in baking powders and self-raising flours. It is made by mixing gelatinised starch paste with sufficient lactic acid to yield a product containing about 46 per cent. of the acid and roller-drying the paste at 125-137° C. *in vacuo*.

Maize starch is used to manufacture vinegar, the process being carried out on the same principle as that by which barley-malt vinegar is produced. The analytical figures for phosphorus and nitrogen given by maize vinegar are much below those generally accepted for a genuine vinegar from barley malt, whereas the figure for the extract and the original total solids are considerably higher.⁸⁸

Extract, or sugar, of malt is widely used as a dietary preparation for the treatment of enfeebled digestions, and is administered as a strengthening accessory in conjunction with cod-liver oil, iron compounds, or quinine. It may be prepared by heating potato starch with water, adding 1-3 per cent. of malt extract, cooling, then adding a further 4-7 per cent. of 'green' malt, and carrying the reaction to the required stage.

The American Diamalt Co.⁸⁷ prepares a proprietary foodstuff by the following method: Maize starch is converted to dextrin by a preliminary treatment with hydrochloric acid in the usual manner. Hot water is then added to give a solution containing from 10-30 per cent. of solid matter, after which it is cooled to 75° C. and the pH value adjusted to between 4.7 and 5.2. An addition of diastase is made and the reaction allowed to proceed for 15 minutes, thereupon the mass is heated to 100° C. for 10-15 minutes, followed by cooling to 70-75° C., at which temperature it is maintained and more diastase added. This stage is allowed to continue until a portion of the solution withdrawn from the bulk gives a brown coloration with iodine solution. The solution is finally concentrated to a syrup of sp. gr. 1.39. This product consists principally of amylopectin, and 24-27 per cent. of maltose, calculated on the concentrated syrup.

Baking Powder. Starch has been used as a comparatively inert

filler in a number of preparations. One such product is that known as baking powder which is added to the materials used to make bread, cakes, etc., in order to leaven the product, i.e. to give off a certain amount of gas during the baking process and thus distend the mass to a honeycomb structure. One brand on the market is said to contain some 40 per cent. of rice starch, and in the U.S.A. maize starch is widely used, indeed baking powder manufacture represents not only one of the largest outlets for corn starch for prepared food purposes but constitutes one of the major applications for which starch is not used for its paste or gel-forming property. W. Gallay and A. C. Bell⁹⁰ have made a thorough study of the effect of potato, maize, wheat and rice starches in combination baking powders under various conditions of storage, and find that stability depends largely on particle size so that rice, wheat, maize and potato starch mixtures were in that order of stability. Again, small wheat granules were found to be better than large granules, and finely-powdered wheat starch better than the coarsely-ground starch. The difference in stability imparted by the various starches becomes more marked as the particle size of the acid component decreases. Those interested in this problem are referred to the full details given in the original paper.

S. Mendelsohn⁶ has presented an excellent account of the function of starch in baking powder media. He points out that rice starch is more costly than other commercially available starches and often contains residual adsorbed alkali which would affect the taste, but this would not be a drawback in baking powders. Wheat starch 'fines' have granules of approximately the same size as those of rice starch and are as efficient as the latter for stabilising purposes. Corn starch, however, keeps the constituents of the baking powder separated more efficiently than other starches and this efficiency is so marked that it outweighs the effect of the greater surface which is presented by this starch and which makes for greater moisture absorption than is the case with rice starch. It is interesting to note that maize-starch granules have an average size which is very close to the mean granule size of the other starches mentioned above.

Good, dry corn starch has for many years been employed in this type of work and looks likely to maintain this position in the face of competition from other agents suggested as fillers in patent literature, especially as the suggested substituents are in most cases, more expensive in use.

Maize starch dried to 5 per cent. moisture content can act as a moisture 'acceptor' and will preferentially absorb and adsorb

about 7 per cent. or more of its weight of moisture in atmospheres of high humidity. Thus it not only separates the acid and gas producing components but also keeps them in a drier state thus reducing any tendency to premature reaction. The latest starches for this purpose are treated with oxidising agents before drying during manufacture to remove those agents responsible for the development of odour.¹³³ Under controlled conditions this treatment gives a free-flowing starch.

In the above case it will be seen that a balance has to be struck between the surface area per unit mass, which affects the adsorption of moisture and hence the stability of the reactive mixture, and the granule size, which governs the effective separation of the components of this reactive mixture. Rice starch and wheat 'fines' present low surface areas, wheat starch a much higher area, whilst maize starch has an intermediate value, but the particle size of the latter affords a more efficient protective effect on the particles of the constituents of the mixture.

A final point of interest about the treated maize starch mentioned above is that its free-flowing property, or 'mobility', is directly proportional to its apparent volume per unit weight so that the more mobile the starch the less the weight of powder required to fill a given sized packet, the better the flow of the baking powder, the greater the free space in the mixture and therefore the better the separation of the components, all important points in packaging of baking powder.

Pastes, sauces, and gravy powders are other culinary adjuncts which are sometimes thickened with starch.

Confectionery. In the manufacture of the so-called *clear-* or *hard-gums* in the *confectionery trade*, the actual vehicle for the glucose, colour and flavouring essences has long been gum senegal. Recently, however, a few firms have turned their attention to replacing this substance by starch, either the soluble or the ordinary variety. Satisfactory results are stated to have been obtained, but the choice of starch appears to be as important as the manufacturing process, no particular trouble being experienced, although long boiling times are generally required. The nature of the product is a function of the formulation used, the cooking and the finishing procedures. Jelly-beans, gum slices or gum drops may be made by the use of thin boiling starch as the sole colloid present. By boiling out most of the water and casting the starch jelly a tough chewing product is obtained but shorter cooking times or lower cooking temperatures gives a 'shorter' textured product, due to the presence of more water, the familiar gum drops or gum slices.

For gum drops tapioca, sago and maize starches have been used, a thin boiling variety of the latter gaining wide acceptance due to its good gelling properties, especially in the 40 to 60 fluidity range, and the lower hot paste viscosity which allows better evaporation and pouring. Tapioca produces gums which have a tendency to 'flop' on storage, i.e. to collapse and also possesses stringy characteristics which lead to difficulties in pouring, the flow of the gum into the mould not breaking abruptly after the mould is filled and the kettle moved to the next mould. The gums are therefore connected by thick threads of gum or are distorted. Sago starch has good gelling properties, but although it produces clear, bright gums at the outset these soon become dull and cloudy after ageing.

Fairly good clear-gums can be made from maize starch which has been converted to a fluidity higher than 60 preferably by the low temperature, acid conversion process of Meisel.¹³⁴ Such gums are rather soft, however, whilst chlorinated maize starch gives a clear gum of low gel strength. If, however, the starch is oxidised by calcium peroxide by the process patented by R. W. Kerr¹³⁵ an exceptionally clear gum drop of high gel strength is obtained. Starch may also be used in Turkish Delight, and is used in the manufacture of pastes and panned sweets either as an ingredient or adjunct in such processes as making moulds.

In making the clear-gums, the syrup is run into moulds and dried for several days. The moulds are formed by indenting the required shape in a packed mass of maize starch. After the gums have been dried to the correct moisture-content, the whole mass, gums and starch, are tipped out on to sieves, the gums being retained while the starch falls through; it is collected and compressed again in trays ready to receive another impression to serve as a fresh mold. The condition of the molding starch is very important. Maize starch dried to a low moisture content and blended with a little edible oil is usually employed, the oil addition being made to increase the capacity of the starch to receive impressions. It should be cleaned and dressed regularly, with additions of new starch to replace losses, so that the general condition of the starch is always uniform. Where possible, starch that has contained 'short-stoved' work should be used next time for longer stoving, as this course assists to keep the starch dry. In this manner good work should be in a fit condition for crystallising with nothing more than a light brushing.

Salad Dressings. N. I. Kozine¹¹¹ has found that the inclusion of potato starch in mayonnaises increases the stability, and allows a reduction in the oil-content without affecting the stability.

The oil-in-water type of emulsion, the so-called mayonnaise type, has long found favour as a salad dressing. It is generally made by emulsifying vinegar into salad oil with the aid of egg-albumin and mustard together with other less important ingredients. Salad mayonnaise may be prepared using starch in the place of the more expensive stabilising agents and the product contains less oil, for the same viscosity characteristics, than the older type of product. They are thus considerably cheaper to make and in some cases may have a dietetic advantage where, for some reason or another, the consumer is allergic to one of the constituents of the older type.

Starch is a poor emulsifying agent when used to prepare the oil-in-water type of emulsion and its use for emulsifying vegetable oils has been dealt with by Goikhman.^{136, 137} With salad dressing the water-in-oil type is largely used and a poor emulsifying agent for an oil-in-water system is not necessarily poor for a w/o type.

The function of starch in a salad dressing is primarily one of increasing the viscosity and stability of the dispersed phase and the physical characteristics of sols and gels from individual starches assume importance. As discussed elsewhere in these pages some starches give 'stringy' gels, others give 'short' gels and the various starches differ in the ease with which their gels may be broken down by mechanical treatment, the action of dilute acetic acid and/or by heating with sugar, a prominent constituent of many of the newer salad dressings. Some starches will not gel in the presence of oils and may develop a pronounced, syneresis with separation of a water phase.

Thus it is unlikely that any single starch will possess all the advantageous properties required and none of the bad, so that mixtures of starches are generally used. As maize starch is fairly stable to acetic acid and once the organised structure of its gel has been broken down the resultant mass is fairly stable to further mechanical treatment it suggests itself as a suitable candidate for this type of work. It requires the addition, however, of tapioca or some other non-cereal starch, which are too fluid to be used on their own, to increase the water-retention, a property in which unmodified maize starch is deficient. Thus the common practice is to use a mixture of maize and tapioca starches in proportions of each varying from 67-33 per cent. Such variations are necessary as the equipment for emulsification varies from factory to factory and adjustments in the formulation must be made according to the emulsifying efficiency and the type of the apparatus.

Starch in the Baking Industry.—The properties of the starch present play an important part in every process connected

with bread-making. Ordinarily it is regarded as forming the source of carbohydrate which is first acted upon by the diastase present in the flour, after which the sugar so produced serves as the fermentation medium for the yeast which is added. Only a small amount of the starch takes part in this sequence. The various terms such as strength, stability, fermentation tolerance, tolerance to mechanical treatment and tolerance to oxidising agents as applied to flour or dough have been well dealt with by Blish¹¹⁷ to whose work readers interested in this branch are referred.

Moisture Absorption by Dough.—Wheat starch in an atmosphere saturated with water vapour at 21.5° C. absorbs at least 36 per cent. water⁷ and assuming that only the water is reduced in volume when starch swells. H. Rodewald⁸ has calculated that it is under a pressure of 2,821 atmospheres in fully imbibed starch granules. A. Maurizio⁹ cites the work of Boutrouse, who has calculated that the distribution of water between the starch and gluten in flour is very nearly the same. Flours containing a higher proportion of gluten require more water in doughing and the distribution will be somewhat different.

In hard wheats the starch is present embedded in a relatively large amount of gluten and very few 'free' granules can be observed. In soft wheat flours, on the other hand, the gluten masses enclose less starch and a larger proportion of the starch granules are 'free'. These granules are readily accessible to and can readily be saturated with moisture. Thus the amount and the freedom of the starch in a flour plays a part in determining the moisture absorption although its influence is probably less than that of the gluten. If the absorptive powers of two starches in two samples of flour are different it follows that the water absorption will be affected.

Starch granules injured by the grinding processes swell more in cold water than do uninjured granules, and a flour that has been severely ground therefore shows an increase in moisture absorption over a flour made from the same grain but less severely milled.^{10, 11} It should be noted that another factor entering into the greater activity of overground flours is the more thorough freeing of diastase present and the more intimate contact brought about between the diastase and starch. The gluten also contributes to this increase as its properties have been somewhat altered also, but when the grinding has been very severe the injury to the gluten is excessive and its moisture absorption decreases. Now injury to the starch granules has another effect inasmuch as the diastase which is present can act on badly injured

granules in the same way as it does on gelatinised starch. Mangels¹² considers that variation in the diastatic activity of a flour is largely dependent on the susceptibility of the starch granule to attack by the diastase, so that a flour with damaged granules will ferment quicker than one in which all the granules are intact. Jones,⁹⁶ has shown that the mechanically damaged starch which is produced during milling is the controlling factor in the diastatic activity of a flour, and the 'maltose figure' is proportional to the amount of mechanically damaged granules resulting from any milling process. In practice this has led to over-grinding of flours considered to be deficient in diastase as suggested by Alsberg.² It should be noted, however, that some workers consider that grinding wheat in too dry a state leads to the excessive formation of damaged granules, which become water-soluble, and that such flours show instability and poor keeping properties.

The Influence of Other Physical Properties of Starch on Baking Quality.—Le Clerc and co-workers,¹³ Shollenberger and Coleman,¹¹ and L. H. Pulkki¹⁴ have studied the effect of different sized granules of normal flour on the baking properties. By bolting they obtained fractions of coarse, intermediate and fine particle size, the intermediate grade having the best baking qualities. E. Grewe and C. H. Bailey¹⁵ found no correlation between the relative baking qualities and the size of the starch granules. E. Giacanelli,¹¹² however, considers that granule size does have an influence on the baking properties. They count the number of starch granules ranging from $2-5\mu$ and those over 5μ in a homogeneous suspension by a microscopical counting chamber and express the two counts as a ratio. They claim that the greater the ratio of fine to coarse granules the better the baking properties of the flour. E. Berliner and R. Rüter¹⁶ found that the saccharification of starch and the flour from which it was derived was parallel but Swedish and Manitoba samples differed. The role of saccharification of the starch in baking will be discussed more fully below.

A number of workers have proposed to use viscosity measurements of flours under various conditions as an index of the baking quality of the flour. Lüers and Ostwald,¹⁷ for example, propose to use the viscosity of a thin boiled flour suspension as an index of this property. The gluten would be altered by this treatment and further differences in the particle-size distribution of the starch granules alone would give similar differences in the complete absence of gluten. There are great differences between strong and weak wheats by this method, but this method gives only a partial view of the problem.

A. Tasman¹⁸ considers that useful information can be obtained by determination of viscosity in the presence of increasing amounts of acid and plotting the differences in viscosity to form a curve.

A. K. Kuhlman¹⁹ examined the viscosity of starch washed from the various samples of wheat and tried to obtain some correlation between the figures obtained and the baking properties of the whole wheat. He prepared gels of different concentrations from the dried and powdered starches and found the viscosities of the gels from the different starches to vary. Those from soft winter wheats, which showed better baking qualities, gave starches which yielded gels having higher viscosities than starches from soft summer wheats of poorer baking qualities. Good samples gelatinised when treated with 0.4-0.5 per cent. caustic soda solution but poor samples required an alkali concentration of 0.7 per cent. This worker plotted the pasting curves of the various starches when treated with alkali and the samples from wheats of good baking properties were characterised by a sharp upward bend in the curve when the concentration of the alkali reached 0.2-0.3 per cent. This indicates that at this concentration of alkali an abrupt increase in the degree of peptisation of the starch takes place. On the other hand, starch from poor wheats did not show this effect, even at the higher concentrations of alkali.

A. Schulerad²⁰ had previously suggested following the viscosity of the starch paste as a means of determining the suitability of rye flour for bread-making and pointed out that the properties of the starch vary with variety and age of the flour. Buchanan and Nadain²¹ consider that the size of the starch granules in wheat flour is an important factor in determining the strength of the flour, inasmuch as the starch in the strongest wheats was found to have the smallest granule size. Alsberg and Rask²² first thought that the difference in the viscosities of starch gels from various wheat samples might be varietal rather than due to the location of growing, but their work later convinced them that the answer was not so simple as significant differences in viscosity were found between starch gels prepared from different samples of the same variety of wheat. In general, winter-wheat starches gave higher viscosities than those prepared from summer-wheats, a fact confirmed by A. K. Kuhlman. Had these workers also determined the gel-strength of the pastes they prepared it seems likely that, in view of Woodruff's work, better correlation between the figures might have been obtained. C. H. Bailey²³ has designed an apparatus similar to that of Caesar in order to measure the relative plasticity of pastes and doughs and to deter-

mine the effect of unit additions of water on the consistency of the dough. In another apparatus elaborated by this worker⁹⁷ the dough is extruded under pressure through a hole in a cylinder, the rate of flow being taken as an index of plasticity. The log rate of flow is a linear function of the water used in making the dough. Very precise temperature control is required with this method.

Vail and Bailey⁹⁸ have re-investigated the question of the proportion of water in dough which exists in the 'bound' state. They make use of an apparatus in which the dielectric properties of the dough are measured. They conclude that 35.5 per cent. of the water in dough exists in the 'bound' conditions as against the figure of 51.4 per cent. calculated by Skovholt and Bailey,⁹⁹ using a freezing-point depression method.

Some workers maintain that flours with similar water adsorptions may lose very different amounts of moisture during baking, and it is possible that the state and character of the starch present exerts an important effect on the moisture loss. A point in favour of this view is the effect of adding potato flour, or starch, which gives a moister appearing loaf. Potato starch, as is well known, behaves very differently from wheat starch on heating with water. The latter gives a mass of swollen granules but the former yields a large amount of colloiddally dispersed material and a larger number of fragmentary particles from the outer sacs of the starch granules.

From what has been said it is obvious that starch does play a definite role in the baking properties of flour, but it must be remembered that this role is subordinate to the part played by the gluten. As discussed in Chap. 10 on the staling of bread the same statement would appear to hold true, whilst the action of the amylases present also has an extremely important bearing on the suitability of a flour for bread-making and baking processes. A number of workers^{113, 114} have attempted to assess the functions of the starch and gluten respectively, on the baking quality of the bread by separating both gluten and starch from good and poor baking quality flours, mixing the separated components in varying combinations and proportions and noting the behaviour on baking of the 'reconstituted' flours. Harris and Sibbett^{113, 114} consider that differences in properties influencing baking qualities, which are apparently inherent in starches from the different varieties of wheat, may be related to injury to the starch granules during milling. The causes of such dissimilarities may be largely heritable, but they present evidence which suggests that environmental conditions are also involved. These differences, as far as variety are

concerned, tend to show that certain wheats which have been viewed with suspicion in respect to baking strength have glutens which yield loaves of inferior volume as compared to glutens separated from wheats commonly considered to be of superior baking strength. Some of these superior wheats apparently have starches which produce loaves of relatively high quality where used in starch-gluten blends. Their work tends to show that starch and gluten in wheat have complementary roles to play but the subject still awaits further work and cannot be further discussed here. The staling of bread is discussed in Chap. 10 and also by Platt,⁸⁴ C. L. Alsberg¹⁰⁷ and L. P. Karacsonyi.¹⁰⁸

The Diastatic Activity of Flours.—The baking qualities of flour are influenced in a most important manner by the diastase present. The type and distribution of the diastases are important factors having a very marked influence on the baking qualities of the flour. Other factors which contribute to the diastatic activity of a flour is the extent to which the granules are attacked by the diastase and the proportion of injured granules present, as the latter are highly susceptible to attack.

In the Scotch process of bread-making a portion of the starch is gelatinised by scalding a portion of the flour and is thus rendered more susceptible to diastatic attack. As diastase is colloidal it is not likely to diffuse through other colloids, such as gluten, very quickly, and it is probable that a contributory cause as to why severe grinding apparently increases the diastatic power of a flour is that the diastase is thus brought into intimate contact with the starch by mechanical means and does not have to depend entirely on diffusion to reach the starch. A further factor is that the severe grinding also liberates the diastase that is mechanically held in the various portions of the grain, for its distribution in the wheat is by no means uniform. The β -amylase of the diastase is not readily liberated as some portion appears to be bound with other constituents. Sandstedt¹¹⁹ and co-workers have shown that dilute salt solution greatly facilitates the release of the bound amylase and salt is often added in the course of bread-making. The proteinase, papain, is also effective in releasing the bound amylase^{120, 121} but its use has to be strictly controlled for its action, if permitted to excess, produces undesirable results in the baking quality of the dough. Wheat itself contains a proteinase with papain-like properties^{125, 126} which is activated by reduced glutathione and deactivated by oxidising agents. This enzyme produces first a clot and then liquefaction of the flour proteins so that retention of gas by the

dough is adversely affected, i.e. the 'strength' of the dough is decreased.

Certain baking aids are often added to flour or dough and among these are oxidising agents. As mentioned, the latter have an inactivating influence on the proteinase and this factor contributes to the beneficial effect of the improver. On storage it has been found that the strength of flour is improved, a similar effect being obtainable by chemical means. Kent-Jones¹²⁷ has shown that these phenomena are due to a loss of proteinase activity.

In barley and wheat the scutellum of the embryo, the endosperm and the aleurone layer are the chief points of occurrence of diastase, the amount of diastase probably falling off as one proceeds from the outer to the inner endosperm²⁴ where the quantity is very small.²⁵ H. P. Wijsman²⁶ and Stoward²⁵ have shown that the diastase of the inner endosperm has but low sugar-producing activity. Thus, as this portion of the grain contains most starch, the diastase can only act on it if brought into contact mechanically or by diffusion. S. S. Elizarova²⁷ has found that practically all spring varieties of *Triticum* have a high β -amylase activity whereas the β -amylase of winter varieties is low. This difference in spring and winter varieties was not found in *Hordeum*. The amylase content of flour may thus vary with its source and Eva and Geddes¹¹⁸ have found the diastatic activity to range from 70 to 300 units in some 80 flours.

Early workers considered that the differences in the diastatic powers of flour were determined by differences in diastase content,²⁸ but F. A. Collatz²⁹ found that the starch of strong flours seemed to be more easily hydrolysed than that from weak flours. O. S. Rask and C. L. Alsberg²² were among the first to consider that other factors might play a more important role than hitherto assigned to them, and, later, Mangels thought that the liability of the starch granule to diastase attack played a predominating part on the diastatic activity of a flour. L. A. Rumsey²⁸ considers that starch granules, themselves, show variations in susceptibility to attack, and A. H. Johnson and C. H. Bailey³⁰ have shown that by making starch readily available in the free condition, e.g. by addition of starch to flour, the rate of fermentation is increased. W. E. Stone³¹ holds that the action of diastase cannot be very great as the water present during baking is insufficient to gelatinise the starch in the commonly understood sense of the word,^{32, 33} but the granules may be present in an extremely concentrated gel and in any event have undergone some change as to render them more susceptible to diastase attack.

The chief source of gas in dough is the maltose formed, and A. Ostrovskii³⁴ therefore considers it necessary in some cases to determine the amounts of α - and β -amylase separately (see below). C. R. Jones³⁷ considers that in flours and intermediate stocks the maltose figure is an index of the number of damaged starch granules present. The maltose figure of the coarse particles, which may escape damage in milling, increases markedly after each rolling. In general, the maltose figure becomes higher the harder the wheat. This worker is another who considers that difference in diastatic activity between flours is not necessarily due to different diastase contents, or even to differences in the susceptibility of the starch to diastatic attack, but that the physical hardness of the endosperm plays some part, as this property influences the amount of damage done to the starch during milling (see also p. 321).

As mentioned above Alsberg² has suggested overgrinding wheats deficient in amylase, or that a small quantity of severely overground flour might be added to them, to improve them.

Another method of improving flours deficient in amylase is to add a readily fermentable substrate such as malt¹²⁸ or dextrose syrup.^{129, 130} A large quantity of malt syrup is used for this purpose, but the extract also contains amylase which may produce an undesirable effect. Dextrose syrups are free from this danger and can be produced with a fermentable-solids content of 80-85 per cent.¹³⁰ Pure crystalline dextrose is produced on a large scale in the U.S.A. and finds one of its largest outlets in the baking industry.

L. H. Pulkki¹⁴ considers wheat starch to have an outer, impermeable envelope which resists diastase action and which is not stained with Congo red. Its removal by grinding allows both diastatic attack and staining with Congo red to take place. Gortner and Hamalainen¹⁰⁹ consider the variable susceptibility of raw starch to diastatic attack to be due in part to an outer protein envelope and it will be remembered that Ling has also postulated an outer envelope around starch, his suggestion being it was hemicellulose. The examination of mechanical damage of starch in flour is discussed on page 321.

With the clear recognition of the presence of the two amylases, at least, in diastase, several workers have studied the effect of the individual components on the baking quality of flours and, as will be seen below, very important results have been achieved by Kent-Jones and Amos. E. G. Onishchenko³⁵ finds that an addition of α -amylase to the dough in the course of mixing lowered the quality of the bread, and that the action of α -amylase

can be inhibited by increasing the acidity of the medium.

Z. F. Falunina¹¹⁵ showed that the strength of dough decreased on the addition of α -amylase while stability and elasticity improved. It would appear that the dextrin produced by the action of the α -amylase on the injured or soluble starch present fortifies the dough gluten perhaps by hydration and this effect is pronounced at concentrations as low as 2 per cent. K. N. Chizhova¹¹⁶ has followed the basic changes occurring in the carbohydrate portion of the loaf during baking. Apparently the intensive splitting of starch in the interior of the loaf is due essentially to the action of the diastase but in the crust thermal changes leading to caramelisation of the sugars is the primary change.

Further studies, on the roles of α - and β -amylases in bread-making, have been made by O. E. Stamberg and C. H. Bailey³⁸ on the relation of the overgrinding of flour to dough fermentation, by L. P. Karacsonyi and C. H. Bailey³⁹ on the baking properties of fractions, and on wheat flour by R. M. Sandstedt and co-workers.⁴⁰

Stamberg and Bailey¹²² find that normal flour does not require the addition of β -amylase since such an addition leads to no improvement in quality. They added pure enzyme preparations to flours and found that the addition of α -amylase, brought about a marked improvement of the volume of the loaf at various fermentation times for the dough. Their results support the contention of other workers¹²³ that α -amylase is the more important of the two amylases present. Sandstedt, Jolitz and Blish¹²⁴ consider that the addition of malt to a flour improves it by virtue of the α -amylase content of the malt.

It would appear that in some cases the yeast finds no fermentable sugars necessary for its action present due, not so much to lack of 'free' β -amylase, but to lack of α -amylase which can liquefy the starch and provide a suitable substrate for the β -amylase to degrade to sugars. The addition of α -amylase does not improve all flours and where such lack of improvement is shown lack of β -amylase or resistance of the starch may be the operating factors.

The Chemistry of certain Baking Faults.—In certain goods aerated by yeast and other means a fault is sometimes encountered known as stickiness or streaks in the crumb. Of the bread produced in Eire some 60 per cent. is the so-called soda bread to which soured milk and sodium bicarbonate is added to make a slack dough which is then baked at a relatively low temperature. The trouble of the sticky crumb has been prevalent in Eire since Irish millers have been obliged by law to use a considerable proportion of native wheat, much of which has been somewhat

out of condition and sprouted. In the case of the popular self-raising flour, when the harvest of English wheat has been a wet one, the presence of sprouted kernels has also resulted in a stickiness or streakiness in the cooked goods.

A certain amount of guidance on the process of a flour to give stickiness in the crumb has been obtained by the application of the maltose test devised by Rumsey²⁸ and extended by Kent-Jones⁴¹ who then employed it as an index of the gas-producing power of a flour. The latter worker, expressing his results as percentages, found the maltose figures for English commercial flour to range from 1 per cent. to just over 3 per cent. For a flour to gas satisfactorily during fermentation Kent-Jones has suggested that the maltose figure (determined by Lane and Eynon's method⁴³) should not be lower than 1.5 per cent. or over 2.3 per cent., as flours showing a figure over 2.3 per cent. are liable to give stickiness of the crumb in loaves or other baked goods.⁴² In America the Blish and Sandstedt method⁴⁴ is generally used in which the flour is incubated at 30° C. in a buffer solution and the amount of maltose, as estimated by the alkaline ferricyanide method, is expressed as milligrams per 10 gm. of flour. In England and on the Continent the Kent-Jones method and nomenclature are used.

Many workers, J. G. Malloch,⁴⁵ M. J. Blish, R. M. Sandstedt, and Astleford,⁴⁶ C. F. Davis and D. F. Worley,⁴⁷ W. J. Eva, W. F. Geddes and B. Frissell,⁴⁸ C. F. Davis,⁴⁹ and R. A. Bottomley⁵⁰ consider that there is no exact relation between the maltose figure and gas production but that the former gives useful guidance as to the general gassing power of a flour and the likelihood of those defects due to incorrect diastatic activity developing. Too low a maltose figure generally indicates poor gassing capabilities under certain conditions, and E. A. Fisher, P. Halton and S. F. Hines⁵¹ consider that a maltose figure over 2.3 per cent. indicated a strong trend toward sticky doughs but, as Kent-Jones has pointed out, there are many exceptions to this generalisation.

N. P. Kosmin⁵² suggested that stickiness of the crumb might be connected with excessive enzymic hydrolysis of the starch so that the remaining starch was insufficient to bind all the water present. As dextrins are produced in this enzymic degradation Kosmin suggested a new criterion of flour quality, dextrinising capacity.

Various workers⁵³⁻⁵⁸ find that starch is converted into maltose and dextrin by β -amylase which is, however, without action on raw undamaged starch and only attacks damaged granules.

As a result of α -amylase action only dextrin is produced (see

Vol. I). According to M. J. Blish, R. M. Sandstedt and E. Kneen⁵⁷ there is some doubt whether the latter enzyme alone is capable of attacking raw undamaged starch. As α -amylase is not so thermolabile as the β -form and is particularly active in the region of 64°C ., a temperature which may occur for a comparatively long period in soda bread, considerable dextrinisation may occur during the baking. Thus a comparatively low temperature long-baking period is more likely to produce sticky crumb than a high-temperature, short-baking process in the presence of the same quantity of α -amylase.

This explains why a high maltose figure does not necessarily involve the development of sticky crumb, as a distinctly high maltose figure may occur concurrently with a low α -amylase activity and *vice versa*. It also explains the success of the Kent-Jones 'dextrin figure' test⁵⁹ in forecasting the tendency of flours towards the defect of sticky crumb.

The Kent-Jones test⁵⁹ is carried out as follows: mix 1.25 gm. of flour to a smooth paste in a 6×1 boiling tube with 3 ml. distilled water using a thin glass rod, and incubate for exactly 30 min. at $62^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. At the end of this time plunge the tube into a cold water-bath and allow to remain for 4 min. The flour paste must on no account be stirred or disturbed during the time from the inception of the incubation to the end of the 4 min. cooling period. To the cooled paste add 2 ml. distilled water and mix to a smooth paste, then add a further 20 ml. distilled water, mix and centrifuge. To 10 ml. of the supernatant liquor add 2 ml. of N/10 I sol. and make up to 100 ml. with alcoholic potassium acetate solution (equal volumes of industrial spirit and a solution of 4 gm. potassium acetate in 100 ml. distilled water). Allow to stand 5 min., then filter off the precipitated starch-iodide. Transfer 50 ml. of the filtrate to a glass evaporating dish and evaporate to a volume of 5-6 ml. on the water-bath, taking care not to carry the reduction in volume to below 5 ml. Transfer the liquid to a 250 ml. beaker, using 10-15 ml. of industrial spirit and then add more spirit to make up volume to 100 ml. Allow to stand 1 hour or preferably overnight and filter off the precipitated dextrin on a tared alundum crucible of medium porosity, washing the precipitate with alcohol, and finally ether. Dry for 1 hour at 100°C . and weigh. The result is reported to the nearest 0.5 per cent.

This technique can be applied to soda bread and self-raising flours without modification. D. W. Kent-Jones and A. J. Amos⁵⁹ find that many really good flours give dextrin figures around 5.6.5 or even lower, but a dextrin figure of 10.0 or lower shows the flour will be perfectly satisfactory. Flours showing

dextrin figures in the region of 10-14 may be considered suspect and, depending upon whether they are baked for a long time in a slack oven or rapidly baked in a hot oven, they give unsatisfactory and satisfactory results, respectively. Flours with a dextrin figure over 14 are likely to give trouble, irrespective of the baking conditions.

As previously mentioned it has been the practice of many bakers in the past to add malt syrup to dough to provide a readily fermentable substrate. In such an addition a quantity of amylase is introduced into the system along with the fermentable matter and it may be that many of the poor baking results of the past may be traced to this factor for, as pointed out by Stamberg and Bailey¹²² too much diastase in a dough leads to sogginess of crumb.

The colloidal chemistry of baking has been discussed by W. Heupke,⁶⁰ whilst a review of the progress of research in the staling of bread has been given by W. H. Cathcart⁶¹ and the controlled factors in baking which enhance the staling properties of bread are discussed in Chap. 10. The evaluation of malt products for use in the bread-making industry has been surveyed by H. C. Freeman and W. P. Ford.¹¹⁰

Biscuits, etc.—This subject is dealt with very effectively by R. W. Kerr.¹³² Starch, as such, is used as a biscuit ingredient and finds other uses in biscuit manufacture which will be dealt with later. Arrowroot starch has for long been used in the production of arrowroot 'hard sweet' biscuits and crackers which because of their ready digestability, are suitable for invalids and children. Kerr considers that their reputation rests upon the fact that arrowroot starch was the first starch to be prepared in a state of purity commercially and carried a high price, its semi-tropical origin and the ease of saccharification by saliva which it has been shown to possess.

The basic material of most biscuits and crackers is wheat flour of the 'soft' variety. In order to obtain the best working properties and give the best product such wheat flour is diluted with starch until the protein content of the mixture is from 7.0-8.5 per cent. when sweet biscuits and cracker goods are being made and 8.4 to 10.0 per cent. when making cracker sponges. Mixtures of the lower protein content behave like starch paste when used for baking whereas cracker sponge mixtures exhibit the characteristics of a dough. The dilution could be carried out by the addition of sugar and shortening but the proportion of these necessary to obtain a good result is undesirably high. In the 1916-1919 period maize starch was added to wheat flour to

the extent of even 50 per cent. without too great a debasement of quality, but such a figure is excessively high. According to the protein content of the flour, as received, it may be diluted with 5-20 per cent. of its weight with maize starch, effecting thereby a saving of about 15 per cent. in sugar and shortening for normal biscuits and some 12·5 per cent. saving when making soft batter dough for vanilla wafers.

The starch prevents the dough from becoming stiff and tough in the interim period between mixing and machining and gives a more tender biscuit than when the starch is omitted.

Flours which are hard to handle, i.e. strong flours, may have 5-10 per cent. of a pregelled starch, of the Amijel or Amidex type with a cold water absorption of 10 : 1, added. This addition increases fermentation, gives a smooth running dough, and eliminates distortion of the biscuit during baking, known as 'buckling' or 'cupping'.

Kerr¹³² summarises the advantages of corn starch in biscuit manufacture as follows : (1) improved flavour and enhancement of added flavourings, (2) clearer colour in the interior of the biscuit, (3) saving in sugar, shortening and, in crackers, of yeast, (4) reduction of sticking of finished goods, (5) improved texture, (6) improved bottom face to biscuit.

The character of the flour is particularly important with ice-cream wafers and cornets, a soft flour giving a crumbly product, whilst too strong a flour yields a brittle product. Wheat flour is modified for such goods by the addition, normally of 5-7 per cent., rarely by as much as 15 per cent., of tapioca starch. As much as 40-50 per cent. can be added but this is excessive. Tapioca starch is preferable to maize starch since it gives a better flavoured, more tender but less brittle wafer. The latter property is highly desirable in that it reduces the amount of loss by breakage when packing.

Finished biscuits do not stale unless first allowed to absorb excessive amounts of water since their normal moisture content of 4-6 per cent. is too low for retrogradation of the starch to be predominant. The keeping quality of the shortening is usually the decisive factor. Tapioca and corn starches were, at one time, popular ingredients of biscuit marshmallows imparting 'set' or stability to the product, but starch is now out of favour in this process owing to its tendency to hold down the volume. The Amijel or Amidex products mentioned above are, however, added to the extent of 0·25-0·5 per cent. at the beater as they promote tenderness yet increase the stability of the product due to the increase in moisture content made possible by the gelled starches.

When sugar is powdered it must be soon used or it may form lumps again. This may be prevented by the addition of 1-3 per cent. of maize starch or of white dextrin. The latter may also be used, incidentally, to make ground salt free flowing. The aprons on icing machines are often dusted with maize starch to prevent sticking in a similar fashion to the use of potato starch on certain rubber goods for the same purpose.

The hard, crystalline structure of flat and 'trolley' icings is sometimes broken by the inclusion of tapioca or maize starches which form points of weakness in an otherwise hard mass.

REFERENCES

1. J. A. RADLEY, *Food Manuf.*, 1941, **16**, 89, 105.
2. C. L. ALSBERG, 'The Role of Starch in Breadmaking,' 'Comprehensive Survey of Starch Chemistry,' R. Walton, Chem. Catal. Co. Inc. N.Y., 1928, p. 87.
3. S. WOODRUFF, *J. Agric. Res.*, 1933, **52**, 46.
4. ——— *Trans. Illinois State Acad. Sci.*, 1936.
5. ——— *J. Agric. Res.*, 1936, **52**, 233.
6. S. MENDELSON, *Food Manuf.*, 1938, Oct., 333.
7. H. RODEWALD, 'Untersuchungen über die Quellung der Stärke,' Lipsius and Tischer, Kiel and Leipzig, 1896, 70.
8. ——— *Landw. Vers. Sta.*, 1894, **45**, 201.
9. A. MAURIZIO, 'Die Nahrungsmittel aus Getreide,' P. Parey, 2nd Ed. 1924, **1**, 349.
10. C. L. ALSBERG and E. P. GRIFFING, *Cereal Chem.*, 1925, **2**, 325.
11. SHOLLENBERGER and COLEMAN, *U.S. Dept. Agric. Bull.* No. 1463, 1926.
12. J. G. MANGELS, *Cereal Chem.*, 1926, **3**, 316.
13. LE CLERC, WESSLING, C. H. BAILEY and GORDON, *Operative Miller*, 1919, **24**, 257.
14. L. H. PULKKI, *Cereal Chem.*, 1938, **15**, 749.
15. E. GREWE and C. H. BAILEY, *ibid.*, 1927, **4**, 230.
16. E. BERLINER and R. RÜTER, *Zeit. ges. Mühlenw.*, 1930, **5**, 134, 156; **7**, 63.
17. H. LÜERS and OSTWALD, *Kolloid-Zeit.*, 1919, **25**, 82 and 116.
18. A. TASMAN, *Chem. Weekbl.*, 1930, **27**, 138.
19. A. K. KUHLMAN, *Zeit. ges. Getreid. Mühl. u. Bäcker.*, 1936, **23**, 128.
20. A. SCHULERAD, *Mühlenlab.*, 1926, **6**, 177.
21. J. H. BUCHANAN and G. G. NADAIN, *Ind. Eng. Chem.*, 1923, **15**, 1050.
22. C. L. ALSBERG and O. S. RASK, *Cereal Chem.*, 1924, **1**, 7.
23. C. H. BAILEY, *J. Rheology*, 1930, **1**, 429.
24. F. J. MARTIN, *J. Soc. Chem. Ind.*, 1920, **39**, 327T and 348T.
25. STOWARD, *Ann. Botany*, 1911, **25**, 799.
26. H. P. WIJSMAN, *Rec. Trav. Chim. Pays-Bas*, 1890, **9**, 1.
27. S. S. ELIZAROVA, *Compt. rend. U.S.S.R.*, 1940, **26**, 698.
28. L. A. RUMSEY, *Amer. Inst. Baking*, 1922, *Bull.* **8**, 84.
29. F. A. COLLATZ, *ibid.*, 1922, *Bull.* **9**, 72.
30. A. H. JOHNSON and C. H. BAILEY, *Cereal Chem.*, 1925, **2**, 95.
31. W. E. STONE, *U.S. Office of Exp. Sta.*, 1896, *Bull.* **34**, 1.
32. WHYMPER, *3rd Rept. Brit. Assoc. Advanc. Sci.*, 1920, 61.
33. W. JAGO and W. C. JAGO, 'Technology of Breadmaking,' London, 1881, pp. 81 and 428.
34. A. OSTROVSKIĬ, *Biokhimiya Khlebopecheniya*, 1938, **1**, 23; *Khim. Ref. Zhur.*, 1939, **2**, No. 3, 134.
35. E. G. ONISHCHENKO, *ibid.*, 1938, **1**, 39; *Khim. Ref. Zhur.*, 1939, **2**, No. 3, 61.

36. D. W. KENT-JONES, 'Modern Cereal Chemistry,' 3rd Ed., 1939, Northern Publ. Co., Liverpool.
37. C. R. JONES, *Cereal Chem.*, 1940, **17**, 133.
38. O. E. STAMBERG and C. H. BAILEY, *ibid.*, 1939, **16**, 319 and 330.
39. L. P. KARACSONYI and C. H. BAILEY, *ibid.*, 1930, **7**, 571.
40. R. M. SANDSTEDT, C. E. JOLITZ and M. J. BLISH, *ibid.*, 1939, **16**, 780.
41. D. W. KENT-JONES, 'Modern Cereal Chemistry,' 1st Ed., 1924, p. 255, 264.
42. — *ibid.*, 2nd Ed., 1927, p. 360.
43. J. H. LANE and L. EYNON, *J. Soc. Chem. Ind.*, 1923, **42**, 32T.
44. M. J. BLISH and R. M. SANDSTEDT, *Cereal Chem.*, 1933, **10**, 189.
45. J. G. MALLOCH, *ibid.*, 1929, **6**, 175.
46. M. J. BLISH, R. M. SANDSTEDT and G. R. ASTLEFORD, *ibid.*, 1932, **9**, 378.
47. C. F. DAVIS and D. F. WORLEY, *ibid.*, 1934, **11**, 536.
48. W. J. EVA, W. F. GEDDES and B. FRISSELL, *ibid.*, 1937, **14**, 458.
49. C. F. DAVIS, *ibid.*, 1937, **14**, 74.
50. R. A. BOTTOMLEY, *ibid.*, 1938, **15**, 509.
51. E. A. FISHER, P. HALTON and S. F. HINES, *ibid.*, 1938, **15**, 363.
52. N. P. KOSMIN, *ibid.*, 1933, **10**, 420.
53. J. S. ANDREWS and C. H. BAILEY, *ibid.*, 1934, **11**, 551.
54. J. W. READ and L. W. HAAS, *ibid.*, 1936, **13**, 14.
55. E. MUNZ and C. H. BAILEY, *ibid.*, 1937, **14**, 445.
56. M. J. BLISH, R. M. SANDSTEDT and D. K. MECHAM, *ibid.*, 1937, **14**, 605.
57. M. J. BLISH, R. M. SANDSTEDT and E. KNEEN, *ibid.*, 1938, **15**, 629.
58. P. S. OUGRIMOV, *Biochem. Zeit.*, 1935, **282**, 74.
59. A. J. AMOS and D. W. KENT-JONES, *Cereal Chem.*, 1940, **17**, 265.
60. W. HEUPKE, *Kolloid-Zeit.*, 1939, **89**, 29.
61. W. H. CATHCART, *Cereal Chem.*, 1940, **17**, 100.
62. O. W. CHAPMAN and J. H. BUCHANAN, *Ind. Eng. Chem.*, 1930, **18**, 190.
63. L. H. LAMPITT and N. GOLDENBERG, *J. Soc. Chem. Ind.*, 1940, **59**, 748.
64. ANON, *Chem. Age*, 1940, 267.
65. E. J. THOMAS, *Food Manuf.*, 1940, **15**, 33.
66. MOORE and PARTRIDGE, 'Analysis of Food and Drugs,' 4th Ed., 1918, p. 105.
67. J. WRIGHT, *J. Agric. Res.*, 1932, **45**, 543.
68. BARKER, *Proc. Roy. Soc.*, 1933, **112B**, 316.
69. — *D.S.I.R. Food Invest. Board Rept.*, 1931, p. 78. H.M.S.O.
70. — *Proc. Roy. Soc.*, 1936, **119B**, 453.
71. APPLEMAN and SMITH, *J. Agric. Res.*, 1936, **53**, 557.
72. BARKER, *D.S.I.R. Food Invest. Board Rept.*, 1936, p. 193. H.M.S.O.
73. F. E. DENNY and N. C. THORNTON, *Contrib. Boyce-Thompson Inst.*, 1940, **11**, 290.
74. LANGWORTHY, *U.S. Dept. Agric., Bull.* 468, 1917.
75. M. D. SWEETMAN, *Maine Agric. Exp. Sta. Bull.*, 383, 1936.
76. WINTON and WINTON, 'The Structure and Composition of Foods,' Vol. II, Chapman & Hall, London, 1935.
77. RATHSACK, 'Der Speisewert der Kartoffel,' Berlin, 1935.
78. McCANCE and WIDDOWSON, 'The Chemical Composition of Foods,' H.M.S.O., 1940.
79. CARPENTER, *J. Nutrit.*, 1940, **19**, 415.
80. M. D. SWEETMAN, *Amer. Potato J.*, 1933, **10**, 169.
81. PERSONIUS and SHARP, *Food Res.*, 1938, **3**, 513.
82. BARMORE, *ibid.*, 1937, **2**, 377.
83. A. DUMANSKI, *Kolloid-Zeit.*, 1933, **65**, 178.
84. PLATT, *Cereal Chem.*, 1930, **7**, 1.
85. U.S.P., 1,913,776.
86. U.S.P. 1,910,344.
87. AMER. DIAMALT Co., E.P. 382,517.
88. E. S. JAMIESON, *Analyst*, 1915, **40**, 106.
89. E. V. MCCOLLUM and O. S. RASK, U.S.P. 1,771,342, 22/7/1930.

90. W. GALLAY and A. C. BELL, *Canad. J. Res.*, 1936, **14B**, 204.
91. SINGH and MATHUR, *Ann. Appl. Biol.*, 1937, **24**, 469.
92. WRIGHT, *U.S. Dept. Agric. Tech. Bull.* **507**, 1936.
93. McCANCE, WIDDOWSON and SHACKLETON, *Med. Res. Counc. Spe. Rep.*, Series No. 213, 1936.
94. J. M. NELSON and R. AUCHINCLOSS, *J. Amer. Chem. Soc.*, 1933, **55**, 3769.
95. NIKOLAEV, *Bull. Acad. Sci., U.S.S.R., Biol. Ser.*, 1939, p. 899.
96. C. R. JONES, *Cereal Chem.*, 1940, **17**, 133.
97. O. E. STAMBERG and C. H. BAILEY, *ibid.*, 1940, **17**, 37.
98. VAIL and C. H. BAILEY, *ibid.*, 1940, **17**, 39.
99. SKOVHOLT and C. H. BAILEY, *ibid.*, 1935, **12**, 321.
100. C. VON SCHEELE, *Med. Kgl. Lantbruksstyrelsen*, 1930, No. 283, 5; via. *Chem. Abs.*, 1931, **25**, 1702.
101. T. CHRZASZCZ, *Polish Agric. Forestal Ann.*, 1931, **25**, 45. (In German, 57 and 59.)
102. B. LAMPE, *Z. Spiritusind.*, 1931, **54**, 235.
103. C. VON SCHEELE and G. SVENSSON, *Landw. Vers. Sta.*, 1931, **112**, 1.
104. — and J. RAMUSSEN, *ibid.*, 1936, **127**, 67.
105. W. TAEGENER, *Deut. Zuckerind.*, 1937, **62**, 69.
106. SPROCKHOFF, *Z. Spiritusind.*, 1930, **53**, 35.
107. C. L. ALSBERG, *Wheat Studies*, 1936, **12**, No. 6.
108. L. P. KARACSONYI, *Z. Unters. Lebensm.*, 1928, **56**, 479.
109. R. A. GORTNER and C. HAMALAINEN, *Cereal Chem.*, 1940, **17**, 378.
110. H. C. FREEMAN and W. C. FORD, *J. Soc. Chem. Ind.*, 1941, **60**, 6.
111. N. I. KOZINE, *Maslab, Jir, Delo*, 1937, **13**, 28(3); *Chim. et Ind.*, 1938, **40**, 975.
112. E. GIACANELLI, *Ann. Tecn. agrar.*, 1943, **15**, 1; *Chem. Zentr.*, 1943, **11**, 1761.
113. D. H. HARRIS and L. D. SIBBITT, *Cereal Chem.*, 1941, **18**, 585.
114. — — — *ibid.*, 1942, **19**, 763.
115. Z. F. FALUNINA, *Akad. Nauk. U.S.S.R. Inst. Biokhim*, Sbornik, 1942, **3**, 4, 18. (In English.)
116. K. N. CHIZHOVA, *ibid.*, 1943 (via C.A. 1943, 5500).
117. M. J. BLISH, *J. Amer. Dietetic Assoc.*, 1938, **14**, 123.
118. W. F. GEDDES and W. J. EVA, *Cereal Chem.*, 1935, **12**, 402.
119. R. M. SANDSTEDT *et al.*, *ibid.*, 1937, **14**, 17.
120. S. JOZSA and H. C. GORE, *Ind. Eng. Chem.*, 1932, **24**, 95.
121. J. S. FORD and J. M. GUTHRIE, *J. Inst. Brewing*, 1908, **14**, 65.
122. O. E. STAMBERG and C. H. BAILEY, *Cereal Chem.*, 1939, **16**, 42.
123. M. J. BLISH, R. M. SANDSTEDT and E. KNEEN, *ibid.*, 1938, **15**, 629.
124. R. M. SANDSTEDT, C. E. JOLITZ and M. J. BLISH, *ibid.*, 1939, **16**, 780.
125. A. K. BALLS and W. S. HALE, *J. Assoc. Offic. Agric. Chem.*, 1935, **18**, 135.
126. H. JORGENSEN, *Biochem. Z.*, 1935, **283**, 134.
127. D. W. KENT-JONES, *Cereal Chem.*, 1934, **11**, 57.
128. L. A. RUMSEY, *Amer. Inst. Baking, Bull.*, 1922, **8**, 84.
129. R. W. KERR and N. F. SCHINK, *Ind. Eng. Chem.*, 1941, **33**, 1418.
130. J. K. DALE and D. P. LANGLOIS, U.S.P. 2,201,609, 1940.
131. R. W. KERR, H. MEISEL and N. F. SCHINK, *Ind. Eng. Chem.*, 1942, **34**, 1232.
132. R. W. KERR, *Chemistry and Industry of Starch*, Academic Press Inc., N.Y., 1944.
133. R. W. KERR, U.S.P. 2,052,308, 1936.
134. H. MEISEL, U.S.P. 2,231,476, 1941.
135. R. W. KERR, U.S.P. 2,268,215, 1941.
136. N. C. GOIKHMAM, *Farmatsiya*, 1939, **10**, 10.
137. — — — *Khim. Referat. Zhur.*, 1940, **5**, 109.

ADDITIONAL REFERENCES

- J. G. MALLOCH, *Cereal Chem.*, 1926, **3**, 316. (Factors affecting diastatic activity of wheat flours discussed.)

- J. G. MANGELS and C. H. BAILEY, *Ind. Eng. Chem.*, 1933, **25**, 456. (Relative viscosities of wheat starches.)
- E. MUNZ and C. H. BAILEY, *Cereal Chem.*, 1936, **13**, 427. (Relation of amylase activity to gassing rate.)
- O. NELSON and G. A. HULETT, *J. Ind. Eng. Chem.*, 1920, **12**, 40. (The moisture-content of cereals.)
- R. M. SANDSTEDT *et al.*, *ibid.*, 1937, **14**, 17. (Factors governing diastasis in wheat flour.)
- R. C. SHERWOOD and C. H. BAILEY, *ibid.*, 1926, **3**, 163. (Control of diastatic activity of wheat flour.)
- C. L. ALSBERG, *ibid.*, 1927, **4**, 485. (Role of starch in flour.)
- J. S. B. HUTCHINSON, *Nat. Assoc. Review*, 13, Supplement, 1936. (Keeping qualities of bread.)
- C. H. BAILEY, 'The Chemistry of Wheat Flour,' Chemical Catalogue Co., New York, 1925.
- E. G. BAYFIELD, *Cereal Chem.*, 1934, **11**, 121. (Evaluation of flours by physical and baking tests.)
- H. J. BROWNLEE and F. L. GUNDERSON, *ibid.*, 1938, **15**, 257. (Oats and oat products.)
- J. BURTT-DAVY, 'Maize, Its History, Cultivation, Handling and Uses,' Longmans, Green & Co., London, 1914.
- F. A. COLLATZ and O. C. RACKE, *Cereal Chem.*, 1925, **2**, 213. (Effects of diastatic and malt extracts on doughs.)
- J. KÖNIG and F. BARTSCHAT, *Zeit. Unters. Nahr. Genussm.*, 1923, **46**, 321; Abstr. in *Analyst*, 1924, 187. (Estimation of rye in wheat flour.)
- O. E. STAMBERG, *Cereal Chem.*, 1939, **16**, 769. (Surface area of starch as a factor in water absorption of doughs.)
- Y. NEMOTO, *Rev. alimentar.*, 1940, **4**, No. 33, 5. (A study of toxicity of bread from manioc flour.)
- A. A. FULLER, U.S.P. 2,317,752. (Modifies starch for food purposes by hypochlorite treatment in presence of nitrogenous body, e.g. gelatin or urea. Short, smooth, viscosity-stable pastes obtained from product.)
- DEUTSCHE MALZENA GES., F.P. 844,572, 27/7/1939. (Oxidised starch for food purposes.)
- F.P. 844,571, 27/7/1939. (Treatment with alkaline H_2O_2 to obtain a tasteless product from potato-starch.)
- STÄRKEFABRIK VEGRITZ GES., G.P. 706,314. (Cl. 53k. 2.01), 17/4/1941. (Edible starch from potato starch. Treat several hours at 40-58° C. with weak acid containing aliphatic alcohol sulphonate as wetting agent.)
- K. SCHLIELER, G.P. 705,822, 1941. (Grate potatoes, free from juice, make acid with H_2SO_3 inoculate with enzyme and store in drained containers.)
- F. M. PORODKO, *et al.*, *Voprosy Pitaniya*, 1939, **8**, 109. (Effect of mode of cooking on the accessibility of starch in potatoes to amylase.)
- J. BARKER, B.P. 542,125, 15/3/1940. (Potatoes cooked, mashed, dried to water content of 45-55 per cent, pressed at 60° C. in watertight vessel until homogeneous, disintegrated and dried to give edible powder.)
- WIRTS. VER. DEUTS. STÄRKE IND., G.P. 739,632, 19/8/1943. (Pudding starch from 50 per cent. potato starch suspension heated at 55-57° C. and pH 5.5-6.6.)
- G.P. 739,716, 1943. (Potato starch treated with alkali until, when alkali is removed, a paste is obtained which is readily cut.)
- H. M. SCHOPMEYER, U.S.P. 2,431,512, 25/11/1947. (Tapioca-like pudding preparation from waxy maize starch.)

CHAPTER 10

THE ROLE OF STARCH IN BREAD STALING*

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I. Why Bread Staling is a Problem

Critical food shortages during World War II and consequent demands for food conservation only serve to re-emphasise the importance of bread staling as a problem in world economy. In 1946, Government reports¹¹⁹ indicated that despite starvation in other parts of the world and attempts to outlaw consignment-selling, countless loaves of day-old bread were still being discarded by the baking industry or sold as a livestock feed in the United States. Nevertheless, the ban on consignment-selling effected a considerable reduction in the amount of stale bread which was returned in 1945; it is estimated that there was a saving of about 465,467,000 loaves.¹⁴⁴ In 1942, moreover, when consignment-selling was the general practice, return of stales was asserted to have been responsible for waste equivalent to 250,710,000 loaves of bread.¹⁴⁴ Staling, however, is by no means purely a contemporary problem. In 1917, the U.S. Food Administration estimated that the return of stale bread accounted for an annual loss of more than 600,000 barrels of flour equivalent to 2.7 million bushels of wheat.⁵ In normal times, staling is of considerable concern to the baking industry and annual losses have been estimated at 3 to 4.7 per cent. of total production.^{163, 181} Besides such costs to consumers and bakers, there is the additional vast and complicated problem of supplying the armed forces, especially in times of war. The desirability of bread in field rations has been repeatedly emphasised by overseas reports. Bread was the food most readily accepted over long periods of time by the troops, and the development by the U.S. Army Quartermaster Corps of a method of canning white bread was of major importance.^{89, 188} Although such canned bread remains palatable for several months,⁵⁰ it eventually 'firms up', develops a colour and gives a dry, pulpy sensation when eaten. Vitamin

* This chapter is based on a review and annotated bibliography of the scientific and technological literature on bread staling conducted by the authors in co-operation with the Quartermaster Food and Container Institute for the Armed Forces, Chicago, Illinois. This review, entitled 'The Role of Starch in Bread Staling', was published as *Quartermaster Corps Report*, 17-10, 1940.

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losses may become significant also, as it is known that thiamine losses are greater the higher the temperature and the moisture content during storage.^{29, 153}

While principally an economic problem, bread staling also presents definite social aspects since bakery workers must do much undesirable night work in order to supply the consumer with fresh bread early in the day. The well-known researches of Katz and Verschaffelt from 1912 to 1916 were first carried out with the hope of finding methods of retarding staling so that night work might be eliminated in Holland.¹¹⁰

II. Meaning of 'Bread Staling'

Staling, as it is applied to bread, is a generic term covering a number of ill-defined changes that occur in bread as it ages. Consumers judge staleness by direct perception, which provides a subjective estimate that probably represents an unconscious integration of many factors. As bread ages certain phenomena are readily apparent: the flavour and aroma change (probably through loss of volatile constituents), the crumb becomes firmer, crumbles more readily and feels harsher to the tongue. These gross changes are doubtless the result of complex physico-chemical reactions within the loaf. These gross changes and the various underlying reactions, as well as other physical or chemical phenomena which contribute to the subjective estimate, comprise the process commonly called 'staling'.

The following changes have been observed during the ageing of normal bread:^{5, 42, 66, 113, 116, 123, 168} (a) The crust becomes soft and leathery; (b) the crumb becomes increasingly tough, hard and eventually crumbly, giving a dry sawdust-like sensation in the mouth; (c) there is a general loss of flavour and development of stale taste; (d) water absorptive capacity of the crumb decreases; (e) the amount of soluble starch in the crumb decreases; (f) the crumb opacity increases; (g) the X-ray spectra of the crumb changes; and (h) the microscopic structure of the crumb changes.

It is apparent from these criteria that the crust and crumb do not undergo the same type or number of changes during ageing and it is often desirable to differentiate between the staling of the crust and that of the crumb.

III. Methods of Evaluating Staling

Since the staling of bread represents a complex transformation which is not clearly understood, it has been customary to evaluate the degree of staleness by measuring one or more of the several

progressive changes which occur in ordinary bread during ageing. A thorough acquaintance with these techniques is necessary for proper understanding of the bread staling literature and the various methods which have been employed will now be discussed.

1. *Compressibility of crumb*: This method was developed to follow hardness changes in crumb during staling. A number of types of apparatus have been designed and used to measure either the distance which crumb can be compressed under a given load, or the force required to bring about a standard compression value.^{9, 12, 53, 75, 157, 164, 165, 198, 201} In the first instance, smaller and smaller deformation readings are obtained with time under a constant load, and it is logical and convenient to call these values 'softness' readings inasmuch as bread softness also decreases with time. However, in the second method, greater and greater loads are required with time to give a standard deformation, and such values may be called simply 'firmness' readings.²³

In the past the majority of the workers have used crumb 'softness' techniques largely as a matter of tradition and also because only recently have the advantages of the crumb 'firmness' methods been pointed out in detail.^{23, 57}

Whether one should use 'firmness' or 'softness' data in evaluating crumb changes might at first thought appear to be purely an academic question. Actually very different results are obtained. 'Softness' units plotted against time, and drawn through a sufficient number of points ordinarily tend to approximate an equilateral hyperbola whereas 'firmness' curves are more nearly linear.^{23, 38, 57, 75, 189, 201} Because of this linearity, the heights and slopes of 'firmness' curves may be compared readily by inspection, and valid conclusions drawn as to relative differences in degree and rate of firming of different breads; that is, the slope of a 'firmness' curve is nearly constant over the usual staling periods, and hence is a direct index of rate of change in firmness. The slopes of 'softness' curves, on the other hand, are complicated functions, depending not only on the rate of change in softness with time but also on the magnitude of the initial 'softness' reading as well. Consequently, 'softness' curves, obtained for two breads having different initial 'softness' readings, cannot be interpreted in terms of the comparative rates of change in softness.²³ Further, even if the initial 'softness' readings on the two breads were of the same magnitude, the task would still be difficult and the results uncertain because the slopes are constantly changing with time.^{22, 23}

Unfortunately, in the past, 'softness' curves have been erroneously interpreted by inspection as though they were straight lines.

This misunderstanding has been a major factor responsible for confusion and controversy in the staling literature. 'Softness' curves characteristically decrease rapidly at first then level off as they approach an artificial staling limit asymptotically.²³ The rapid initial decrease has long led workers to object to this test on the basis that the greatest change in bread 'softness' occurs in the early hours following baking, or at a time when bread is still considered fresh by the consumer.⁴² The fact that 'softness' curves level off comparatively early in the staling period and appear to become approximately parallel explains why so many authors have concluded that their experimental breads were 'staling' at about the same rate as their control or standard bread. It should also be emphasised that in determining 'softness' changes, smaller and smaller values are recorded with time, hence the ability of the instrument to resolve differences becomes a factor; whereas in the 'firmness' method, larger and larger values are obtained with time.

While published data are limited, the 'firmness' test apparently gives results comparable to those obtained when human judges evaluate bread on the basis of the perceptible changes in firmness^{22, 57} as well as consumer acceptability.²⁰³

In addition to the 'firmness' and 'softness' techniques, some attempts have also been made to study crumb elasticity.^{23, 57, 74, 75, 157, 164} Platt¹⁶⁴ subjected bread crumb, three hours out of the oven, to several different loads and found that the deformation varied directly with the magnitude of the load; that is, it followed Hooke's law and behaved as a perfectly elastic body. Other workers since have carried out more complete studies, involving a wider range of stresses and strains and breads of different types and ages, with the resulting conclusion that bread did not obey Hooke's law, especially when fresh.^{23, 189} Recently, Geddes *et al.*,^{74, 75} using a newly designed compressimeter which automatically records curves showing the compression and elastic recovery of bread slices, found that bread slices (0.5 inch thick), three to seventy-two hours of age, recovered completely following application and removal of loads up to 500 g., provided fresh slices were used for each successive load. When the series of loads were applied to the same slice of bread, however, the three-hour-old bread slices did not recover completely for deformations above 7 mm. Force-deformation curves obtained on canned white bread by Bice and Geddes²³ indicated that as bread aged the relationship between force and deformation became linear up to higher and higher loads. Considering these results in conjunction with those of Geddes *et al.*,^{74, 75} above,

leads to the conclusion that bread crumb does not behave as a perfectly elastic body but as a plasto-elastic solid. In the case of fresh crumb, plastic flow is an appreciable factor in the compression which is observed, but as the bread stales and becomes rigid, presumably by the establishment of a three-dimensional structure through the formation of cross linkages, the possibilities for plastic flow become more and more restricted and the behaviour of the bread more closely approaches that of a purely elastic body.²³ It would, therefore, be expected that the elastic regain of stale bread would be greater than that of fresh bread; moreover, any treatment which would increase the softness would tend to cause the bread to deviate more from Hooke's law and, by increasing the possibility for plastic flow, would yield bread exhibiting lower elastic recovery from the application of stress.

It should be emphasised that cereal chemists and physicists use the term 'compressibility' in an entirely different sense and this has caused some misunderstanding in the recent bread staling literature.^{23, 28} In physics, 'compressibility' is the reciprocal of the bulk modulus,⁸⁴ the modulus of elasticity which applies only in cases where the force or pressure is brought to bear equally on all sides, or over the whole surface of the test object.⁶⁸ The bulk modulus is not applicable to bread compressimeter measurements where the pressure or force is applied only to two faces of the bread section. The most appropriate modulus of elasticity in such cases, provided Hooke's law is followed and shearing does not occur, is Young's modulus (the modulus of compression or stretch) in which by definition, equal force is exerted at opposite ends of the test object.⁶⁸ Young's modulus = force per unit area/change in length per unit length; that is,

$$Y = \frac{F/A}{e/L} = \frac{FL}{Ae}$$

where, in the case of bread, F is the force applied; A , the effective area of the pressure plate; e , the decrease in slice thickness; and L the initial slice thickness. Young's modulus, stress per unit strain, has been used in the cereal chemical literature^{158, 16} as a modulus of compressibility. Since crumb 'firmness' readings are force values, they are directly proportional to Young's modulus, or to the modulus of compressibility as defined in the cereal chemical literature.

It would appear from present knowledge that bread is too complex a substance to satisfy the assumptions necessary for the strict application of an elastic modulus. Since the stress-strain

curves cannot be readily interpreted, the change in firmness of bread crumb is best given simply as 'firmness' units (force required to give a particular deformation with a slice of definite thickness). These 'firmness' units in comparison with those obtained on normal or standard bread would have direct meaning in terms of the 'squeeze' test employed by the consumer to ascertain how firm the bread feels. A standardised crumb 'firmness' technique, based upon a careful laboratory study, has been proposed by Crossland and Favor.⁵⁷

2. *Absorptive capacity of crumb*: During staling, the ability of the crumb to imbibe water decreases. This so-called 'swelling power' change has been followed in the laboratory by several procedures in which the crumb is first pulverised in water and the amount of water held by the crumb measured by sedimentation volume,^{100, 113, 114} centrifuged volume,⁴⁸ or increase in weight of crumb sediment after centrifugation of the slurry.^{9, 180} Viscometric methods which are also claimed to measure absorption changes, involve the determination of crumb-dough mixing strength in the Farinograph,^{9, 23, 51, 69, 70} crumb slurry viscosity in the Amylograph⁶³ and the measurement of capillary-flow of a thin, pulverised crumb slurry.^{9, 50, 94, 96}

In applying measurements of sedimentation volume to staling studies, careful consideration must be given to the various factors which may influence the results. For example, studying the effects of chemical adjuncts, the sedimentation height of the crumb particles will depend upon their sedimentation velocity which in turn is influenced by the several variables embodied in Stokes' law of falling bodies.* The adjunct might be adsorbed on the crumb particles and influence their specific gravity, or change the viscosity of the dispersion medium, thus rendering it difficult to interpret crumb sedimentation data particularly when obtained on breads made by different formulas.²³

As a further complication, the sedimentation, viscosity and Farinograph methods give values which decrease with time in a markedly curvilinear manner reminiscent of the 'softness' curves previously discussed.^{69, 165} Consequently, such curves cannot

* Stokes' law of falling bodies:

$$V = \frac{2}{9} \frac{(D-d)}{\eta} G r^2$$

where V = velocity of fall

D = the specific gravity of the falling particle

d = the specific gravity of the medium through which the fall takes place

η = the viscosity of the medium

G = the gravity constant

r = the radius of the particle.

logically be interpreted in terms of rates of change merely by inspection processes.²³ Misinterpretation of such data in the past may well have led to faulty conclusions in many cases.

3. *Soluble starch in crumb* : The amount of so-called soluble starch that can be leached from the crumb with water decrease with the age of the loaf. The method involves water extraction of the water-soluble polysaccharides of the crumb and precipitation by means of alcohol, followed by their recovery and drying.^{9, 110, 180} This procedure is so time-consuming that it is not often used. Here again, caution must be exercised in drawing conclusions when comparing results obtained on different breads. If one bread contains an adjunct capable of forming a water-insoluble complex with the soluble starch, a low or 'stale' soluble starch value would be obtained since the usual amount of soluble starch would not be extracted from the crumb. This might well mean that staling is being partially inhibited because the soluble starch would no longer be free to aid in building up an immobile three-dimensional gel structure.

4. *Crumbliness* : An empirical crumbliness test for bread has been developed^{23, 40, 186} which involves weighing the amount of crumb which erodes from slices of bread of given surface area and thickness when placed upon a gyrating sieve operated for a fixed time under controlled conditions. The crumbliness values increase with time and would appear to be a factor of interest in relation to consumer acceptance. It seems probable that a certain level of crumbliness would be associated with tenderness and ease of mastication whereas excessive crumbliness would be undesirable since the bread would not slice well. It has proven difficult to obtain reproducible results with the crumbliness method.²³

5. *Crumb opacity* : Bread crumb becomes more opaque as bread ages and this change can be followed by measuring the light transmission through the crumb by photoelectrical means.⁷⁸ The change is said to begin about two days after baking and continues until about the tenth day under normal storage conditions.

6. *Enzyme susceptibility* :^{119, 184, 193} Retrograded starch is less susceptible to attack by amylases than freshly gelatinised starch and a convenient method for following the extent of retrogradation has been described ; this involves measurement of the carbon dioxide liberated from a buffered suspension of the bread crumb to which malt extract and yeast have been added.¹⁸⁴ The greatest decreases in starch susceptibility occur during the first 10 to 15 hours after baking in a manner reminiscent of crumb 'softness' and swelling power changes.

7. *X-ray diffraction pattern* : By use of X-rays, Katz^{110, 111, 115, 117, 119} found that fresh bread crumb gave a V-pattern whereas stale crumb gave a B-pattern superimposed upon a V-pattern.* An increase in crystallinity is thereby indicated which provides an interesting parallel to changes taking place in starch pastes during retrogradation. This method has been employed recently by Carlin,³⁶ who reported that the change in X-ray diffraction pattern closely parallels staling predictions based on examination of penetrometer data obtained by use of a modified Bloom Gelometer.²⁰¹

8. *Organoleptic tests* : The difficulties involved in utilising the senses for evaluating staling are numerous and have discouraged their use in favour of the simpler, more quantitative results obtained by the laboratory methods previously discussed. There is a distinct need for carefully planned comparative studies correlating the results of organoleptic tests with those of the physical methods already mentioned.

The various properties of bread which have been used to follow the staling process change at different rates as bread ages. In a comparative study of several measures applied to a uniform lot of commercial white bread over a 72-hour period, Bice and Geddes²³ found that the crumbliness values showed the greatest over-all change followed by crumb 'softness'. The greatest changes in swelling power, crumb 'softness', and soluble starch occur within the first several hours after baking or at a time when the bread is still considered fresh by the consumer.^{23, 42, 110} Crumb 'firmness' and crumbliness values change at a more uniform rate than the above measures.²³ Moreover, compressibility techniques may yield results with bread containing certain ingredients which would lead to opposite conclusions concerning the extent of staling than those which would be reached from a consideration of Farinograph, Amylograph, and swelling power data.^{22, 23, 40, 63, 69} Likewise, Katz,¹¹⁰ after addition of acetaldehyde to bread, found that the swelling power of crumb remained the same as in fresh bread whereas the quantity of soluble starch decreased upon storage.

Investigators who are engaged in devising methods for measuring certain properties of bread and in determining how these properties change as bread ages often tend to assume that each

* While Katz claimed that fresh bread gives a V-type X-ray pattern, E. Niegel (*Z. physik chem.*, A188, 137-159 (1941)) has shown that this V-pattern was due to an alcohol complex, occasioned by Katz' use of alcohol in preparing the bread and starch paste samples. It would therefore perhaps be preferable to say that the starch of fresh bread has an amorphous character, and that a B-pattern develops on staling.

method measures 'the rate of staling' and to argue the relative merits of different methods from this viewpoint. It seems more reasonable to suppose that any one physical or chemical method can measure, at best, only a few of the factors involved in the subjective integrated assessment of staling. Each method can reveal only part of the story. Since there is no *a priori* reason for supposing that the various processes involved in staling take place at the same rate, there is no reason to expect that methods that measure different properties will give identical data for rates of change in the crumb.

It appears that the comparative merits of various objective measures of bread staling can only be determined adequately through the use of organoleptic tests made by a panel of experts under a strict statistical control. The panel would hardly be able to make quantitative estimates of staleness, that is, to judge whether one sample was two or three times as stale as another; but given a series of bread samples, it should be possible to rank them at least roughly in order of 'staleness'. The physical or chemical measurements that place the same series in most nearly the same rank order as the panel may then be said to be the best objective method of measuring staleness.

Until a study of this nature is made, it seems that methods now in use must be accepted for what they actually are; namely, methods of measuring the change in some property or properties of the bread with time. That some properties, such as crumb firmness and crumbliness, are related to staling is a reasonable inference but to suppose that any one method actually serves as a measure of the whole process seems unjustified on the basis of our present knowledge.

IV. Theoretical Aspects of Starch and its Retrogradation

Most of the changes occurring during bread staling have been attributed, at one time or another, to alterations in the starch.^{5, 51, 100, 106, 107, 110, 155} For this reason, numerous studies have been carried out on the ageing of starch pastes in an effort to learn the basic mechanism of staling. Unfortunately, until fairly recently, chemists have been handicapped by the confused state of the literature concerning the structure of starch.

The development of better methods of fractionating starch^{177, 179, 210} into two molecular components each having definite properties, and improved means of characterising these fractions,^{18, 210, 213} were major steps in the clarification of the starch picture. The advent of this new knowledge makes possible a better understanding of the problem of retrogradation

of starch and bread staling. Before discussing the past work on bread staling, therefore, some of the pertinent theoretical aspects of starch gelatinisation and retrogradation will be briefly considered.

Starch occurs in nature as microscopic birefringent granules, or spherocrystals. When heated in excess water at increasing temperatures, the granules gradually swell and eventually lose birefringence, usually over a range of about 10° to 15° C.⁸ The point at which all birefringence finally vanishes is known as the gelatinisation temperature and is in the neighbourhood of 65° to 70° C. for most starches. Katz¹¹⁰ referred to this as first order gelatinisation. If the temperature is raised to 100° C. (Katz's second order gelatinisation), the granules become highly swollen, transparent and fragile, and a viscous paste results. Heating this paste at higher temperatures as in an autoclave at, say, 120° C., results in the disintegration and dispersal of the granules.¹⁷⁹

Starch granules, moreover, may be swollen and dispersed in cold water upon the addition of certain chemicals,^{34, 80, 147, 148, 149} or following drastic mechanical injury such as in ball milling.^{1, 7, 138, 191}

When starch granules are heated in excess water, the degree of swelling appears to be a function of temperature,^{110, 112} that is, the granules reach a certain swelling stage typical for a given temperature and within reasonable time limits do not swell more until the temperature is raised.^{5, 110} If, however, insufficient water is present, then swelling may be greatly inhibited.¹²⁹ For example, Katz¹¹⁰ has shown that the starch in the interior of bread while subjected to temperatures of 90° to 100° C., during baking, because of insufficient water swells only to a degree normally reached at about 70° C. in excess water.

Starch granules prior to gelatinisation have a crystalline structure as indicated by X-rays,^{110, 117} and the polarising microscope. Characteristic X-ray spectra are given by various starches:^{117, 120, 174, 175} cereal starches (e.g. corn, waxy corn,⁸⁸ wheat, rye, barley and rice starches) exhibit an A-pattern; potato, chestnut, horse chestnut and certain curcuma starches, a B-pattern; while tapioca, arrowroot and 'real sago' show a C-pattern (intermediary between A- and B-patterns). At the gelatinisation point, or during Katz's first order gelatinisation, birefringence is lost and X-rays indicate a less crystalline state as evidenced by a V-pattern† for wheat and rye starches,^{117, 126} and an amorphous pattern for potato starch.¹²⁶ In excess water at 90° to 100° C., an amorphous X-ray pattern is obtained for all of these

† See footnote on p. 209.

starches.^{110, 117} In other words, the process of gelatinization appears to be one of molecular disorganisation.

If the temperature of the paste is lowered to room temperature, then the equilibrium shifts so that the starch tends to go back to a less soluble, less hydrated state characteristic of the lower temperature.^{100, 110, 117, 127} The X-ray spectrum shows a return toward a crystalline state as a B-pattern is obtained.^{110, 117, 126, 132} This tendency of starch pastes to return towards a more aggregated, less soluble state has been termed retrogradation, and is exemplified by the well-known gel formation, increased opacity and syneresis which occur on cooling and ageing.*

Starch is now generally regarded as being composed of a mixture of two structurally distinct kinds of molecules—linear and branched chain types, usually known as amylose and amylopectin, respectively.^{83, 152, 177} Since the terms amylose and amylopectin were used in a different sense in the earlier literature, they are somewhat misleading. Schoch¹⁷⁷ has used the terms 'A-fraction' and 'B-fraction' to denote the linear and branched molecular fractions of starch. However, in this review the two sets of terms are used interchangeably.

When an autoclaved starch sol is allowed to cool in the presence of polar organic materials such as a mixture of amyl alcohols, butanol,¹⁷⁹ long chain fatty acids^{142, 177, 182} or certain nitro-paraffins,²¹⁰ the amylose or A-fraction is selectively precipitated as a crystalline complex with the precipitant and may be separated from the amylopectin or B-fraction by centrifugation.

Among other differences, amylose stains blue with iodine and shows a marked tendency to retrograde from aqueous solutions, whereas amylopectin stains a red-violet with iodine and is usually said to show little tendency to retrograde.^{83, 87, 88, 177} More will be said of this later.

The ratio of amylose to amylopectin varies for different starches, and, of course, accounts for some of the variations in properties among starches of different genera and species. The following table indicates the amount of amylose present in a few typical starches. (See Table XI on page 213.)

The waxy starches contain only traces (if any) of amylose, and are said to consist entirely of branched chain molecules. Waxy starch stains red-brown with iodine and its pastes behave in a manner reminiscent of amylopectin sols.

* The term 'retrogradation' was first used by L. Lindet (*Bull. soc. chim.*, (3) 27, 634-639 (1902)) to describe the changes occurring in the starch of bread during staling. This pre-dates use of the term 'retrogradation' by Maquenne and Roux.

TABLE XI

<i>Starch</i>	<i>Amylose (%)</i>	<i>Reference</i>
Pea (Garden, wrinkle-seeded)	60-75	86, 156
Easter lily	34	18
Sago	27	18
Wheat	24-26	18, 180
Corn	22-29	18, 179, 210
Popcorn	23	18
Potato	22	18, 179
Waxy barley	0	18
Waxy corn	0	18
Waxy rice	0	18
Waxy sorghum	0	18

Comprehensive studies on retrogradation carried on by Whistler and co-workers^{209, 211} are of particular interest in connection with bread-staling. Autoclaved (120° C.) sols of defatted starches were allowed to retrograde and the effects of temperature, concentration and starch types on the rate and extent of retrogradation studied. In agreement with earlier work by Schoch,¹⁷⁸ the rate of retrogradation of defatted corn starch at 1° C. was found to increase almost exponentially with increase in concentration of the sol over a range of 0.5 per cent. to 3 per cent. The extent of retrogradation was about the same for all concentrations. The rate and extent of retrogradation decreased with rise in temperature. Addition of sodium sulphate to autoclaved sols increased the rate of retrogradation. If starch were not defatted, the rate but not the extent of retrogradation was retarded. Defatted corn starch and heat-moisture-treated potato starch retrograded rapidly and extensively, the retrograded material having practically the same amylose-amylopectin ratio as the original starch. Defatted wheat starch showed some tendency to fractionate during retrogradation. In the case of potato, tapioca and arrowroot starches, a fractionation was apparent, as retrograded material from the first 5 days contained 93 per cent. amylose for potato and tapioca, and 82 per cent. for arrowroot. Retrograded fractions of sweet potato starch, however, had essentially the same amylose content as the original starch.

In order to study retrogradation in starch pastes at concentrations similar to the moisture-starch relationships which prevail in bread, Schoch and French¹⁸⁰ followed the ageing of 40 per cent. corn starch (defatted) and 50 per cent. wheat starch (defatted) pastes, respectively. Upon cooling, both pastes set to hard, almost cartilaginous gels. The amount of soluble starch was determined by a modification of the Katz test for crumb solubles.¹⁸⁰ The amylose content of the solubles was measured by a modified potentiometric iodine titration method.²¹⁰ Less soluble starch was extracted from the pastes than from bread

crumb and the soluble starch from bread crumb appeared to contain a much lower proportion of amylose. The difference between iodine sorption and quantity of solubles from bread and starch, respectively, was attributed to amylase action since these differences were not apparent after the addition of 0.2 per cent. malt extract to the starch. Defatted 50 per cent. waxy corn-starch pastes formed hard gels upon standing three to six days. Heating to 100° C. effected a return of the gel to a soft, glutinous state. Soluble starch could not be determined because the slimy character of the solubles prevented filtration.

There is a slight tendency for amylopectin molecules to 'retrograde' spontaneously from dilute starch sols on cooling and ageing. This tendency toward aggregation and dehydration can be hastened by refrigeration.²¹⁵ In fact, sols or pastes of starch, waxy starch, and amylopectin, all form spongy masses upon slow freezing and thawing after which much of the water may be readily expressed mechanically.¹⁴³ When examined with a polarising microscope, the network of all these sponges appears highly birefringent.^{143, 215}

Schoch and French¹⁸⁰ mention the spontaneous separation of small spheres or discs from amylopectin sols when refrigerated in the presence of a 20 per cent. aqueous solution of one of the lower alcohols such as methanol, ethanol or isopropanol. These spherules gave a faint B-pattern by X-ray diffraction methods and swelled rapidly at 53° to 57° C., going into solution at 100° C. These two properties, as Schoch and French point out, are interesting corollaries to some of the changes which occur during the refreshing of stale bread crumb by heat. These investigators suggest that the aggregation of the amylopectin may occur by coacervation in the sense that there is a separation of a concentrated phase in the form of liquid droplets with subsequent crystallization within the droplets.

On the basis of X-ray studies, Katz¹²¹ found an acceleration of retrogradation when small amounts of 15 per cent. alcohol solutions were added to starch pastes. Droplets, similar to those described by Schoch and French, have been observed without the use of alcohol by others when dilute (e.g., 0.5 per cent.) starch sols or pastes were frozen slowly and allowed to thaw.²⁰⁴ The resulting spherules swelled in water with heat.

The changes taking place in a starch paste upon cooling and ageing, have been attributed by some^{11, 34, 35, 73, 133, 134, 208} to the formation of hydrogen bonds or bridges, through water molecules between donor and acceptor groups of neighbouring amylose or amylopectin molecules. At temperatures below the gelatin-

isation point or especially at or near 0° C., more of such bonds are supposedly made than broken at any given instant so that the molecules may become more closely associated.

The branched configuration of amylopectin probably is not as conducive to close alignment of molecules, hence hydrogen bonds would be expected to be fewer and of a hit or miss nature. On the other hand, in the case of amylose, the linear type molecules would be expected to be closely associated and more difficult to disperse whereas retrograded amylopectin would, because of its looser aggregation, seemingly be more readily dispersed. That this is actually the case is familiar knowledge to those who have attempted to disperse these materials in the laboratory. Gel formation has been attributed therefore, to the possible formation of a three-dimensional molecular network whereby colloidal units are held together by hydrogen bonding as described above.

During retrogradation the water-holding capacity of the starch gel lessens due to aggregation, and visible leakage (syneresis) may occur depending on the gel concentration.⁵ Kerr¹³³ has suggested that with the formation of each hydrogen bridge between starch hydroxyls, one or more molecules of water may be freed. When heat is applied to retrograded starch, dispersion is thought to result from excitation and consequent rupture of the hydrogen bonds. According to Caesar³⁴ hydrogen-bonding may explain the action of chemical gelatinising agents on starch since Buswell, Gore and Rodebush (quoted by Caesar) showed with infra-red absorption studies that the 4 co-ordinated structure of water was apparently partly destroyed by 4 Molar concentrations of NaI, NaSCN, NaBr, etc. Dissociation of such large aggregates of water molecules would allow better penetration by the water into the starch aggregates.

Recent investigations by Sair and Fetzer¹⁷³ indicate that the sorptive capacity of a starch may be a measure of its degree of molecular association. By treating air-dried potato starch for three hours with steam at a pressure of five pounds per square inch, its properties are significantly altered so that the X-ray pattern, paste characteristics and water-sorptive capacity resemble those of a cereal starch. The starch granules are not gelatinised or injured by the heat-vapour treatment. The properties of the cereal and pith (i.e. sago and arrowroot) starches subjected to heat-moisture treatment were modified only slightly in comparison with the change taking place in the instance of potato starch.

V. Studies Contributing to Staling Theories

To the average consumer, bread staling perhaps still appears to be largely a drying out process; however, as early as 1853, Boussingault²⁷ showed that bread readily staled even when sealed in a glass tube to prevent moisture loss. He further showed that the stale bread could be refreshed merely by warming at 70° C., and that staling and refreshing of the sample could be repeated almost indefinitely provided no mould developed. He therefore postulated that stale bread is not different from fresh because of water content, but as a result of a change in the molecular state that begins upon cooling and is maintained unless the temperature is raised above a certain level.

According to Alsberg,⁵ like views were held by Von Bibra and others who conducted similar experiments on rye and barley breads. Further, Von Bibra found that bread could no longer be refreshed by heat if the moisture content fell to 30 per cent. or below, unless first remoistened.

A different mechanism was proposed by Horsford (quoted by Alsberg⁵) in which he suggested that loaf moisture is redistributed during staling. The freshly baked crumb structure was described as being made up of a thin gluten reticulum with adherent starch, the former being dehydrated and the latter in a soft hydrated state. Upon cooling, and staling, it was assumed that the gluten absorbed water from the starch causing the latter to become dry and vitreous and hence contributing to crumb rigidity. On reheating, the moisture was assumed to be redistributed as in fresh bread.

Balland (in Platt¹⁶⁴) and Lehmann (in Alsberg⁵) are said to have observed that stale crumb did not have the ability to swell and imbibe water like fresh crumb. However, Lehmann found that when the inhibition was carried out at 40° to 60° C., or if the stale crumb was first warmed, then the absorption of moisture was almost equal to that of fresh crumb. This work of course, served as a foundation for subsequent swelling tests¹¹⁰ used to measure staling. He found also that pieces of crumb, upon drying, shrink over a period of about four days but continue to lose water after that time.

Boutroux, according to Alsberg⁵ was probably the first to suggest that staling results from the separation of an insoluble derivative of starch. Without laboratory evidence he hypothesized that amyloextrin separated as a solid when bread cooled. Alsberg⁵ points out that no one has ever found such a compound in bread crumb.

Lindet (in Alsberg⁵) observed a decrease in soluble starch (not

amylodextrin as Boutroux had assumed), in bread crumb upon staling, which he termed 'retrogradation'. Finding similar changes in gelatinised starch, he concluded that the starch in bread crumb loses its moisture through retrogradation rather than by absorption by the gluten, and that this change was responsible for bread staling.

From 1912 to 1916, extensive studies on staling were undertaken by Katz¹¹⁰ with the objective of eliminating the night work of Dutch bakers. Katz developed quantitative methods for the determination of swelling power and soluble starch based upon the earlier findings of Balland, Lehmann and Lindet. Crumbliness was estimated by brushing the fingers lightly over the crumb. Later, he developed a test for softness or compressibility. It was found that during staling, the greatest changes in softness, swelling power and soluble starch occurred within 9 to 10 hours after baking, whereas crumbliness was not definite until about 24 hours.

Crust staling was shown to be a simple process involving the absorption of moisture from the atmosphere and (or) the loaf interior. The complex changes of the crumb were not found in the crust.

If sufficient moisture was present, all kinds of bread (Katz excluded zweibach and Swedish bread) were found stale on the basis of the four tests employed.^{104, 110} Katz showed that bread would not stale if too little or too much water were present.^{110, 121, 130} Thus, it was discovered that bread could be held at any given stage of staleness by drying or submerging in water. By these methods and the addition of a little disinfectant, bread was maintained in fresh and stale states, respectively, over a period of four months.¹¹⁰

Katz, therefore, concluded that an optimum water content is necessary for staling. Although at a loss to explain adequately why excess water should prevent staling, he suggested that staling may involve the interaction of two or more molecules with consequent loss of water and that excess moisture might restrain this removal of water. Katz's findings on optimum moisture content have been partly verified and extended by Geddes and co-workers⁷³ in studies on bread samples having crumb moistures of 16.4, 22.3, 27.1, 30.5, 33.2 and 36.8 per cent., respectively. The swelling power of bread crumb stored at 16.4 per cent. moisture remained constant while the hydration capacity of the crumb stored at 22.3 to 36.8 per cent. moisture decreased with time, the rate of decrease being greater with an increase in the moisture content at which the crumb was stored. In excess

water, the crumb showed a slight increase in swelling power over a four day period.

When moisture relationships were optimum for staling, Katz^{100, 101, 110, 124} found that the degree of staleness was a function of the temperature. Bread crumb was held at various temperatures for 24 to 48 hours under controlled moisture conditions and the bread remained fresh at 60° C., or above; half-stale at 40° C.; completely stale at -2° C.; and fresh at -10° to -185° C.^{99, 110} Staleness was evaluated by tests for crumbliness, swelling power and soluble starch. As has been previously mentioned in the section on retrogradation of starch, similar temperature-moisture equilibria were observed during the gelatinisation and cooling of starch pastes.¹³¹ In the case of starch pastes, however, no crumbliness changes were attained. Katz^{110, 122} points out that this is in agreement with his ideas since crumbliness had been attributed to the shrinking of starch granules away from the gluten reticulum in bread crumb. Verschaffelt,^{205, 206} on the basis of microscopic observations, reported that during staling the starch granules in crumb shrink and develop surrounding air spaces thus relaxing their previous close union with gluten.

Katz^{107, 110} extended his retrogradation studies to include raw starches from wheat, sago, rice, potato, barley, maize, oats, lentils and maranta. In these researches, 50 per cent. pastes were heated at 100° C., thus approximating the moisture and temperature relationships in bread-making. Katz was then able to make the generalised statement that not only do various breads stale, but also other kinds of starches besides wheat starch.

Later,^{110, 111, 115, 117, 119} Katz reported a difference in the X-ray spectra of fresh and stale bread. Fresh crumb gave a V-pattern whereas stale crumb exhibited a B-pattern superimposed on a V-pattern. Thus on cooling and ageing, there is a tendency toward a more crystalline structure. Applying the same tool to 50 per cent. wheat starch pastes, he found a similar return to a B-pattern. Thus, he concluded that bread staling results from retrogradation of the starch. He considered that both starch components, amylose and amylopectin, are affected by retrogradation.¹²⁸

Katz^{108, 110} found that staling was inhibited by the use of certain adjuncts such as soluble, volatile aldehydes and a number of organic bases. Tests were carried out by placing 10 grams of bread crumb on a layer of glass beads in a flask, then introducing 0.05. ml of the liquid to be tested between the beads by means of a pipette. The flask was stoppered and allowed to stand 24 to 48

hours after which staling was evaluated by determining the swelling power and the quantity of soluble starch. Acetaldehyde, propionaldehyde iso-butylaldehyde and acrolein prevented changes in hydration capacity and in the quantity of soluble starch for periods of several days to several weeks. If these volatile chemicals were removed by an air-stream, the normal changes in these properties proceeded to take place. Slightly less effective were such alkaline substances as pyridine and dipropylamine. Chloroform and allyl alcohol showed only a weak influence. Acids, esters, ketones, allyl halides, dimethyl and diethyl sulphates had no appreciable effect as inhibitors of staling. Katz assumed that the inhibitors formed complexes with the starch thus preventing interaction of hydroxyl groups. As Katz pointed out, however, these particular chemical inhibitors were obviously of theoretical interest only. In these studies contradictory indications were given by swelling power and soluble starch tests. After 14 days in the presence of acetaldehyde, crumb still possessed the swelling power of fresh bread, whereas soluble starch tests indicated total staleness. Katz raised the question whether these tests really measured the same process.

Katz did, nevertheless, develop one method by which bread was successfully kept in an apparently fresh condition overnight.^{103, 105, 109, 110} This method, which involved storage of the bread in a controlled atmosphere of 65 to 75 per cent. relative humidity, served to inhibit crust staling and to delay the onset of crumbliness. The Dutch consumer desires bread possessing a fine texture, hence crumbliness, rather than firmness is the change to which the most objection is raised.

Ostwald (in Alsberg⁵) agreed with Katz that starch is the chief factor in the staling of bread, but disagreed with the retrogradation hypothesis. Instead he ascribed the change in the starch gel to an internal aggregation and dehydration with consequent loss of water by syneresis.

In regard to the mechanism of staling, Fuller⁷⁰ suggested that retrogradation and syneresis of starch gels, and bread-staling changes are perhaps all manifestations of the same phenomenon; namely, a decrease in the hydration capacity of starch gels with time.

According to Alsberg and Griffing,⁶ gluten in bread may not have lost all its colloidal properties as completely as some have assumed. Even after exposure to moist heat at 80° C. for 30 minutes, gluten was found to swell appreciably in weak acid. These conditions, however, do not approximate those prevalent during baking where temperatures of 90° to 100° C. are attained.

In fact, Katz¹¹³ was unable to find any change whatever in the swelling power of gluten in bread during staling. In his studies, he removed the starch from the gluten of the crumb enzymatically and then determined the swelling power of the residual gluten. He also coagulated fresh gluten in boiling water and determined its swelling power and water content immediately, and after two days' storage at 2° to 3° C. Neither swelling power nor water content changed during staling. Stockham¹⁹⁷ also observed that baked gluten does not vary in its hydration capacity with a change in temperature. Incidentally, Katz¹²⁵ has asserted that bread low in starch, such as gluten bread, changes only slightly upon cooling and ageing.

Despite these experiments and apparently without further experimental work, Alsberg⁵ later suggested that the following sequence of changes occurs when bread stales. When the bread comes out of the oven the moisture is distributed in several ways; some occupies the crumb pores as a vapour, some is absorbed in the starch and held by the gluten and the remainder is free to act as a solvent for salts, sugars and the like which are present in the crumb solution. In this fresh state, the starch was said to be soft and the gluten tender. On cooling, the starch gel shrinks and probably the gluten also shrinks slightly becoming harder as it loses moisture to either the starch or crumb solution, or both. Eventually, crumbliness becomes apparent because of strains arising during the change in moisture distribution and unequal drying. Prior to this latter change, however, the starch begins to retrograde. It is not clear on what basis Alsberg makes the assumption that gluten shrinks and loses water during cooling, especially since Katz's experiments yielded different results.

Recently, Esselbough⁶² has studied the chemical changes which occurred in gluten and in whole wheat bread over a 72-hour storage period. He found an increase in pH, in nitrogen-containing compounds and in amino acids after an initial decrease; the titratable acidity and total solids of the aqueous extract likewise increased. Karacsonyi,⁹² while not able to prove experimentally that water of syneresis liberated from the starch gel is absorbed by the protein gel, nevertheless tentatively considered that protein hydration probably occurs. Further physical and chemical studies of possible changes in gluten during staling are merited.

Certain objections to the retrogradation theory were raised by Alsberg^{2, 3} who pointed out that retrogradation of starch pastes is a slow process, whereas staling is comparatively rapid. Further, he emphasised that retrograded starch is not easily dispersed at temperatures which affect freshening of bread. However, Als-

berg's objection regarding the relative rates of starch retrogradation and bread staling is not valid, since Katz¹¹⁰ had already demonstrated the rapid retrogradation and heat reversibility of 50 per cent. starch pastes, a concentration which approximates that of the starch-water system in bread. Indeed, Alsberg later mentioned the rapid retrogradation of concentrated starch pastes which had been gelatinised in the first degree.⁵ Further, Schoch¹⁷⁸ and Whistler and co-workers²¹¹ have also shown that the rate of retrogradation of starch pastes markedly increases with starch concentration.

If, however, Katz's retrogradation theory is interpreted as meaning that staling is due to the retrogradation of amylose,* then, as Hixon⁸⁷ pointed out, bread baked with flour containing waxy starch instead of wheat starch should show little tendency to stale.

Noznick, Merritt and Geddes¹⁵⁹ subsequently baked bread from gluten-starch mixtures, the starch component of which consisted of mixtures of wheat starch with various quantities of waxy maize starch. Complete substitution of waxy maize starch for wheat starch gave loaves which were characterised externally by a shiny, sugary crust and internally by a gummy compressible crumb and excessive shrinkage after baking. Upon storage, the crumb compressibility of loaves containing waxy maize decreased at about the same rate as that of loaves made from mixtures of gluten and wheat starch alone; the swelling capacity of the crumb, however, decreased more rapidly with time when waxy maize starch was present. The authors concluded that at least amylose is not the sole factor responsible for staling and that bread-staling is perhaps associated with changes in the branched chain component of wheat starch.

Recent work by Schoch and French¹⁸⁰ points to a similar conclusion. The soluble starch from crumb was found to have a low iodine sorption by potentiometric iodine titration, hence it was assumed that this fraction consisted principally of branched chain molecules. On this basis and since the quantity of soluble starch decreases during ageing, it appeared that staling was associated with a gradual insolubilization of the amylopectin. Similar studies on 40 per cent. corn starch (defatted) and 50 per cent. wheat starch (defatted) pastes, respectively, revealed that a

* The term retrogradation was at first applied rather loosely to designate the changes occurring in the starch of bread during staling (cf. footnote p. 209); however, more recently others^{5, 87} have used the term as meaning the spontaneous insolubilization of amylose. The insolubilization of the whole starch or of the amylopectin is entirely different with respect to rate, extent and reversibility, hence much needless confusion has resulted in the literature.

lower amount of solubles was obtained from starch than from bread and that these solubles had an iodine sorption capacity substantially lower than that of the original starch. However, when 0.2 per cent. malt dextrin was added to the starch, iodine sorption values and the amount of solubles approached the results obtained with bread crumb. Schoch and French suggested that this reduced affinity in the solubles may be due to the formation of short chain linear fragments from enzymic hydrolysis of amylose. Using 50 per cent. wheat starch (defatted) pastes, Schoch and French then studied the effects of certain adjuncts on swelling power, soluble starch and iodine sorption. It was concluded that probably 'normal amounts of yeast, hydrogenated shortening, salt and protein have little influence on the behaviour of the starch in bread'. Free fatty acid, however, would probably promote staling significantly.

At the beginning of their work, Schoch and French suggested four possible mechanisms of staling based upon the literature; namely, retrogradation of amylose, coacervation of amylopectin, insolubilisation of total starch substance and co-precipitation of starch and protein. At the termination of their researches, they regarded the coacervation (i.e. 'heat-reversible aggregation') of amylopectin as the best explanation of the bread-staling process. This coacervation was attributed 'to intermolecular association between the linear side-chains of branched molecules, a type of aggregation which is much less firm than that involved in the retrogradation of the A-fraction' (i.e. amylose). In support of this hypothesis, they found that removal or modification of these side chains, as by treatment with β -amylase, oxidation or derivatisation, resulted in decreased ability to form coacervates. Further, Samec and Katz¹⁷⁴ by means of X-rays observed that 5 per cent. pastes of Lintnerised potato starch gave only an amorphous spectrum, rather than a B-spectrum.

This type of association through possible hydrogen bonds has also been mentioned by Caesar^{34, 35} and Kerr^{133, 134} and was briefly discussed in the section on retrogradation in this review. Caesar³⁵ indicated that the mechanism of starch association is probably hydrogen-bonding through water molecules although he postulated that such would not be the case for retrograded or vigorously dried starch. (See Vol. I.)

Experiments carried out by Bachrach and Briggs¹¹ also tend to favour this hypothesis, at least in part. Moisture content-relative vapour pressure studies indicated that stale crumb binds 0.01 grams more water per gram (dry basis) than fresh crumb. Likewise, gelatinised retrograded wheat starch bound 0.015

grams more water per gram than gelatinised non-retrograded wheat starch. The corresponding figure for wheat starch amylose was 0.025 grams; and for potato starch amylose 0.035 grams. This very slight increase in bound water ('approximately one molecule for ten glucose units') was considered too small to account for the very large increase in crumb rigidity on the assumption that the water is no longer free to act as a plasticiser. Hence, the data were interpreted as favouring the hypothesis that the increase in crumb rigidity is due to the formation of a three-dimensional structure resulting from hydrogen-bonded cross-links between molecules. The small amount of water additionally bound during the process suggested to the authors, however, that the cross-linkages formed may involve some water molecules as molecular bridges.

Similar conclusions concerning the mechanism of retrogradation of wheat amylose have been drawn more recently by Wands and Briggs.²⁰⁸ Calculation of the change in free energy during the sorption of water by retrograded and non-retrograded wheat amylose yielded results which indicated that hydrogen bonds are involved in retrogradation. On the basis of the over-all experimental observations, it was proposed that molecules of retrograded amylose are held together by bridges of water molecules acting through hydrogen bonds.

In general, the proposed 'hydrogen-bond' mechanism is compatible with the gelatinisation, dispersion and associative changes which are characteristic of starch systems. The asserted inhibition of 'staling' by excess water,^{73, 110, 121, 130} however, seems to be anomalous, since even dilute starch pastes retrograde. More research is required on the effect of excess water on 'staling' rates.

From a practical standpoint, such a hypothesis fosters the intelligent selection of possible adjuncts or starch plasticisers as a means of inhibiting or masking staleness in bread. Kerr¹³⁴ has discussed the theory and action of such plasticisers in producing a variety of useful properties in starch pastes for specific industrial uses. He classifies the known adjuncts according to four possible modes of action:

1. Lubrication, wherein such substances as neutral fat and mineral oils perhaps film over colloidal aggregates thus lessening internal friction of the pastes.
2. 'Complex formation between major constituent and adjunct' to bring about either (a) closer, or (b) reduced polymer-polymer association, Kerr lists borax, sodium

- aluminate, pyroantimoniate, formaldehyde, and acetaldehyde as compounds typical of class (a); whereas chloral hydrate, urea, dicyandiamide and ammonium thiocyanate are said to cause reduced association (class b).
3. 'Complex formation between major constituent and a part of the adjunct, the balance of the plasticiser remaining in the "free state".' Water is included here. Kerr suggests that humectants such as glycerol might be considered here also since they 'tend to maintain water relationships'.
 4. Special complex formation whereby the shape of the colloidal unit may be changed due to changes in the molecular configuration of constituents. Polar fractionating agents—fatty acids, aliphatic alcohols, nitroparaffins, acid amides, etc., are included under this mechanism.

The action of substances in groups 2, 3, and 4 presumably involves the formation of hydrogen bonds at starch hydroxyl groups, the resulting properties depending somewhat upon the structure of the plasticiser through which the bonds or bridges are formed.

In selecting a plasticiser for a starch paste, or in this instance a bread-staling inhibitor, consideration should also be made of the possibility that the 'staling' of the starch may perhaps occur in two places in the bread system:

1. Within the individual starch granules causing them to become more firm.
2. In the soluble starch dissolved in the water medium between the swollen granules or between surface molecules of adjacent granules, thus 'cementing' the granules into a fixed position.

If further research indicates that the latter effect is the basis for the consumer's unfavourable reaction to stale bread, there is considerable hope that its influence may be minimised by the use of soluble adjuncts. If the former action is primarily responsible for staling, then its prevention by incorporation of soluble adjuncts does not appear too feasible.

VI. Technology and Control of Bread Staling Prior to 1947

A number of substances have been proposed as adjuncts to prevent or mask the staling of bread. Such inhibitors will be briefly discussed in this section together with technological

factors, such as baking conditions, which have been suggested as influencing keeping quality. Many of the conclusions are highly controversial, largely because of differences in methods of evaluating staleness, and lack of agreement as to what constitutes staleness. Consequently, in the following survey of the literature, the burden is necessarily placed on the reader to consider carefully in each case the meaning and validity of the 'staling' test which is employed. Particular discrimination is required in those instances where conclusions concerning staling rates are based upon the comparison, by inspection, of highly curvilinear 'staling-time' curves. Unfortunately, the majority of the conclusions have been made on this questionable basis and accordingly many may well be invalid.

Adjuncts said to retard bread staling :

A. *Aldehydes* : As has been brought out earlier, Katz¹¹⁰ found that water-soluble and volatile aldehydes retarded bread 'staling' as determined by swelling power and soluble starch tests. His work has been verified by Fuller,⁷⁰ using 10 per cent. acetaldehyde (by volume), who, moreover, found that there is even a slight increase in water absorption by bread crumb when so treated. He pointed out that the hydration capacity of starch is markedly affected by acetaldehyde at room temperature. Using formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, crotonaldehyde, benzaldehyde, salicylaldehyde, cinnamaldehyde and 2-furaldehyde, Karacsonyi^{93, 95} found that the retarding action of these compounds toward bread 'staling' was proportional to their volatility and solubility in water. He found that some aldehydes change crumb consistency and others cause colour development with the proteins. The starch and probably the fats were unchanged and he found that aldehydes could not be removed as easily from proteins as from starches. Since aldehydes cross-bond starch molecules, it is possible that their action on bread staling may be due to the 'fixation' of an amorphous arrangement by acetal cross linkages between the molecules of starch, thus preventing their subsequent orientation to a crystalline pattern.

B. *Alkaline substances* : It will be recalled that Katz¹¹⁰ observed that pyridine and dipropylamine appreciably retarded changes in crumb swelling power and in soluble starch values upon the storage of bread. Like the aldehydes he investigated, these basic compounds were poisonous or malodorous and hence were of no practical importance for controlling staling. Ott,¹⁶¹ however, was granted a patent on the use of glucosimine to inhibit staling of 'bakery products, coffee, etc.'.

C. *Polyhydroxy alcohols* : Sorbitol²⁰⁰ and glycerol^{39, 140, 141, 190} have been claimed in various patents as bread improvers and staleness inhibitors when small amounts are incorporated in dough prior to baking. Broeg,³¹ however, asserted that there is very little advantage in incorporating glycerol into dough from an economic standpoint ; in fact, it has been shown to have a negative effect on the keeping qualities of canned bread.⁵⁰

D. *Milk and milk products* : Bailey¹³ using crumb 'softness' and swelling power tests found no staleness-inhibiting action by the inclusion of milk products in the bread formula. On the other hand, later workers have reported favourable results using dairy products.¹⁹⁴ Increasing the amount of non-fat milk solids in bread increases the initial softness of the crumb.¹⁶⁵ Light translucency studies^{77, 78} on water and milk breads revealed that increases in crumb opacity were more marked in the case of the water bread, indicating more rapid staling.

E. *Protective colloids* : Attempts to stabilise water relations in bread crumb by the addition of such protective colloids as agar, mayonnaise, and lecithin were made by Bailey.¹³ With the possible exception of agar, none of the substances he tried had any effect on crumb softness or swelling power. Khrustalev and Muserskii,¹³⁵ however, did not find any stabilising action by the addition of 0.5 per cent. agar-agar. More recently^{30, 55, 166} it has been claimed that the addition of lecithin representing about 1.75 per cent. of the weight of shortening employed cuts down the moisture loss from the loaf so that the keeping quality is improved.

F. *Carbohydrates* : In general, the addition of carbohydrates such as arabinose,⁶⁰ xylose,⁶¹ glucose,³⁹ fructose,¹⁶ sucrose,¹⁷¹ acid- or heat-dextrinised starch,^{15, 151} gelatinised starch,^{5, 15} and 5-10 per cent. rye flour⁵ have been reported to favour a softer crumb and hence apparent longer freshness in bread. In one instance, bread to which sucrose was added was reported as being fresher according to compressibility tests after three days than bread made using anhydrous cerelose.¹⁷¹ On the other hand, Bailey¹³ in an earlier study found that no inhibition of staling occurred after additions of invert sugar, a mixture of glucose and sucrose, or dextrinised starch as shown by crumb 'softness' and swelling power tests. He did, however, find that 'staling' was retarded after addition of malt extract. Addition of 3 per cent. potato flour effected an increase in crumb 'softness', but had no influence upon the loss of swelling power.¹³ Kuhlmann and Balasheva,¹³⁷ on the contrary, stated that sugars tend to retard 'staleness' and listed several carbohydrates in the order of de-

creasing effectiveness as follows : maltose syrup, glucose syrup, dextrin, beet sugar, maltose, glucose, control, soluble starch, potato starch. Sandstedt, Jolitz and Blish¹⁷⁶ attribute the dough-improving action of malt extract to the action of the amylases on starch. Brooks³² asserts that the action of malt extract in delaying 'staling', is due to the hygroscopicity of the malt sugars and usually results in fresher bread than that obtained with other sugars. In support of Sandstedt, *et al.*,¹⁷⁶ is the claim that Badex (a commercial blend of dextrin and sugars from cereal carbohydrate conversion) owes its 'staleness' retarding effect to the increase in starch liquefaction which occurs in bread-making.¹⁹⁵

G. Soybean flour : Addition of soybean flour to bread dough has been claimed to retard the staling of the baked bread.^{25, 26, 81, 196, 198, 202} This adjunct is said to be more effective with breads made from weak flours than with those made from strong flours.¹⁹⁶ According to Hafner,⁸¹ staleness is retarded due to stabilisation of moisture relations and inhibition of breakdown of shortening and other fats because of the antioxidant effect of soy flour phosphatides.

H. Shortening : Addition of shortening to dough brings about an increase in the compressibility ('softness') and tenderness of crumb in the resulting bread,^{5, 165, 212} but does not retard staling on the basis of swelling power tests.⁸⁵ The type of shortening has been shown to have a bearing on keeping quality as determined by flavour, peroxide formation and pH determinations.⁷⁹

I. Inorganic salts : Various inorganic salts have been suggested as possible staling inhibitors. High salt content has been said to aid in keeping quality,¹⁶² but has little influence on crumb shrinkage.¹⁸⁵ Magnesium chloride has been included in a canned bread along with glycerol and glucose as a hygroscopic agent to aid in the preservation of the bread.³⁹ Calcium peroxide did not prevent staling on the basis of crumb 'softness' and swelling power tests.¹³

J. Paraffin, beeswax : A bread preservative tried by the British Army¹⁵⁴ consists of 20 parts by weight of 'waxes' (75 per cent. paraffin, 25 per cent. beeswax) mixed in the molten state with 80 parts straight grade flour. In use, 8 lb. of this preservative is mixed with 280 lb. of flour and normal baking methods then employed. The formula was developed to provide emergency rations for isolated troops to whom supplies could be delivered only at irregular intervals. Since no immediate use of the formula is in view, no research has been done to determine possible physiological effects of continuous consumption of such bread.

In warm climates calcium propionate is added to prevent rope infection.

Other technological factors said to have an effect on staling or keeping quality of bread

Flour quality: Baking technologists recognise that one of the primary factors in the production of bread of good keeping quality is the use of flour containing a large amount of high quality gluten.^{5, 90, 212} In the case of bread baked from four flours having protein levels of from 9.6 to 12.6 per cent., it was found that loaves made from the strong flour did not 'stale' as rapidly, as measured by crumb 'softness', viscosity and swelling power tests, nor reach as high a degree of 'staleness' as those made from the lower protein flours.¹⁹⁶ It follows, then, that any factor affecting the strength or quantity of gluten may indirectly have an effect on the keeping properties of bread made from such flours. Actually, as is well known, climate and wheat type do significantly influence gluten properties.⁸² Even 'hard wheat patent flour' consists of about 78 per cent. starch on a dry weight basis,⁵² and the starch also may be affected by environment and heredity, which give rise to noticeable differences in viscosity^{10, 67, 169, 170} and resistance to enzymes.^{4, 145, 146, 192} During storage of flour, improved baking quality, followed by deterioration occurs.⁶⁷ The initial improvement may vary from a short time to several years, depending upon the conditions of storage.

Milling effects: Overgrinding of flour does not cause significant changes in the fermentation rate of the dough or in the keeping quality of the resulting bread according to Karacsonyi and Bailey.⁹⁷ Pulkki,¹⁶⁷ in fact, obtained better loaves from medium fine flour than from coarser or finer products. With reduction of particle size of flour, he found increased water absorption, increase in amylolytic activity and slower development of the dough during mixing. These results are in line with those of Malloch¹⁴⁵ and others^{4, 176, 191} who reported that grinding starch granules decreased their resistance to enzyme attack. Alsberg and Perry⁷ and others^{138, 191, 192} found that grinding injures the granules so that they gelatinize in cold water, or even dissolve if the injury is great enough.

Dough treatment: Alsberg⁵ has generalized that any factor which increases the moisture content of bread seems to favour longer life. Thus slack doughs^{45, 90} and optimum high-speed mixing^{25, 45, 71, 102} are said to have a favourable effect on keeping quality. On the other hand, Hutchinson⁹⁰ pointed out that while over-mixing can give an attractive exhibition loaf of soft

texture, it is likely to taste dry in the mouth and hence be unsuitable from a consumer standpoint. The use of a sponge dough method accompanied by scalding some of the flour has been found to increase the water-binding capacity of the dough and is therefore said to have retarded 'staling'.¹³⁶ Schoonover¹⁸³ found that high absorption aids but slightly in the retention of freshness, as determined by crumb compressibility measurements.

Fermentation: According to Katz¹¹⁸ fermentation at high temperature using an excessive amount of yeast will lead to bread having poorer keeping qualities than that produced after low-temperature fermentation with the usual amount of yeast. Alsberg⁵ suggests as long a fermentation at 22° to 26° C. as is possible without gluten breakdown to lengthen the life of bread. He also suggested the use of 'not too much yeast', and the sponge dough and sour-dough fermentations. Bailey¹³ also found a retarding effect by the addition of 3 per cent. of sour dough. Fuller⁷⁰ observed that bread made with diastatic malt extract had abnormally low Farinograph absorption values (based on the amount of water necessary to give a crumb dough consistency of 500 units) when fresh; and that this value did not decrease with staling. The improving action of malt on certain flour doughs is ascribed to the action of the α -amylase on the starch rather than to protease activity.¹⁷⁶ Yeast quality may be of importance. Alsberg⁵ stated that some English bakers believe beer yeast produces a better-keeping bread than distiller's yeast. In this connection, the legendary keeping quality and flavour of certain Scotch breads are of particular interest.⁷² In former times, 'Parisian' barm (a home-grown yeast) was used instead of compressed yeast, however, distiller's yeast is now largely used. Nevertheless, one of the large bread factories in Scotland has used the former, and claims that as a result, they have a virtual monopoly in the sale of bread in the Hebrides. Keeping quality is very important for this particular trade because three to five days elapse before the bread reaches the consumer. This company states that by actual experiment with two groups of consumers, the long fermentation process 'barm-baked' bread was found to be preferred because of its superior flavour and keeping quality.

According to Butterworth and Colbeck³³ there is no difference in the microscopic structure of dough at different stages of fermentation, although Katz¹¹⁸ claimed that the arrangement of the starch granules changed with the degree of ripeness of the dough.

Oven conditions: There seem to be two schools of thought on the best oven conditions for the production of bread of optimum

keeping quality. One advocates a slow baking at lower temperatures so that relatively little moisture is lost,^{5, 172} while the other considers a high extensive oven heat necessary to gelatinise the starch and form a good crust.^{90, 162} It has been demonstrated in Army field rations that bread baked slowly to produce a thick crust may keep its freshness and palatability 7-10 days after baking.¹⁴

Storage conditions and wrapping : It has been shown by Katz¹¹⁰ and confirmed by numerous others^{13, 56, 171} that bread can be maintained in a nearly fresh condition if stored at 60° to 70° C. under controlled moisture conditions ; however, the method was not considered to be practical because of loss in flavour, development of an off-aroma within 12 to 24 hours and difficulty in controlling the growth of micro-organisms. Fuller,⁷⁰ however, found that bread crumb stales slightly even at 60° C., as indicated by crumb-absorption studies in the Farinograph.

Bread stored at temperatures of -9° C. to -185° C. for variously prolonged periods has been found to retain its freshness from about three days at -9° C.,¹³ to an extreme of 345 days^{41, 43, 44} when packed in tin cans and stored at -22° C. Vacuum-packed samples had better flavour than those packed in air.^{43, 70} A few workers have asserted that samples packed in carbon dioxide retain superior flavour and keep better,^{207, 214} while others have found no benefit from the use of carbon dioxide.^{46, 47} Commercial application of the freezing process in one instance¹⁶⁰ was discontinued because the cost of freezing and storage was found to be 1·25 cents a pound.

Wrapping of bread has been found to prolong shelf life by preserving the aroma and flavour and the softness of the crumb better than unwrapped bread.^{17, 58} Conservation of the moisture is probably the main factor in effecting the greater softness of crumb, since it has been found that unwrapped two-pound loaves stored 6·5 days lost 12·4 per cent. moisture in summer and 10·25 per cent. in winter, whereas wrapped loaves during the same period lost only 0·85 per cent. in weight.¹⁵⁰ The loss in the case of unwrapped loaves was said to occur mostly in the outer 0·5 in.^{69, 151} In some studies^{19, 20, 21} the temperature at which bread was wrapped was found to influence the keeping quality, flavour and odour as judged from a consumer's standpoint. Keeping quality implied freshness and freedom from rope or mould infection.²¹ Bread was wrapped at 114°, 99·9°, 87·5° F. and allowed to cool slowly ; and at 88·1° F. followed by rapid cooling in refrigerator. Bread wrapped at 114° F. was judged to have the best keeping quality but the poorest odour and taste ; that cooled quickly after wrapping at 88·1° F., was rated second in keeping quality.

odour and flavour ; that wrapped at 87.5° F. with slow cooling had the poorest keeping quality but the best flavour and odour ; and bread wrapped at 99.9° F. with slow cooling was placed third on all points.²⁰

The introduction of bread-slicing in the industry has been beneficial according to some¹³⁹ since sliced bread 48 to 60 hours old may feel as fresh to the consumer as unsliced loaves at 24 hours.

It should be emphasized that many of the factors necessary for the formation of bread crumb of good keeping qualities are considered deleterious to good crust qualities. For example, Alsberg⁵ lists the following conditions which are considered necessary for the production of crust of good keeping qualities : high fermentation temperature, much yeast, as little water as possible and a small amount of salt. It would appear that technological attempts to control staling are complicated by the fact that what may contribute to crust of good keeping quality may be detrimental to the keeping quality of the crumb, and vice versa.

As far as adjuncts are concerned, Hutchinson⁹⁰ in 1936 stated : ' Keeping quality is at a maximum in bread made from good flour of ample gassing power, good gluten content and quality with correct absorption, dough manipulation and fermentation. Such bread will benefit little, if at all, in keeping quality through the addition of any of the many substances and proprietary articles which have been recommended from time to time as inhibitors of the staling process.'

Until quite recently Hutchinson's statement concerning the ineffectiveness of so-called staling inhibitors, seemed to be borne out in general by the literature. However, since 1947 a number of commercial emulsifying agents have been found to delay the increase in crumb ' firmness ' as well as the ' set-back ' or retrogradation of starch pastes. Because of the tremendous interest in these so-called ' softeners ', they will be discussed in the next section along with other recent technological advances in the staling field.

VII. Some Technological Advances in the Control of Bread Staling since 1947

Recently, interest in baking and staling investigations has been heightened by the commercial introduction of a number of agents claimed to have some anti-staling action.^{22, 28, 38, 59, 62} In the course of hearings before the U.S. Federal Security Agency in 1948 and 1949 for the purpose of establishing standards of identity for bread and similar baked goods, in the United States, consider-

able controversy has arisen as to whether these adjuncts actually delay the rate of firming or whether they merely soften bread.

In 1947, Favor and Johnson⁶⁴ reported that the inclusion of as little as 0.5 per cent. of polyoxyethylene monostearate in the baking formula exerted a softening action on bread crumb and markedly retarded the development of firmness of the crumb with age. The addition of this emulsifier to starch suspensions raised the temperature at which a detectable increase in the viscosity was registered by the Amylograph but did not prevent complete gelatinization at the higher temperatures. Further, the 'set-back' or retrogradation of starch pastes was inhibited by the presence of this adjunct.

Later, the same authors⁶⁵ presented statistical evidence that breads containing 0.5 per cent. polyoxyethylene monostearate (flour basis) were not significantly softer than control loaves the first day out of the oven although they were markedly so after three days' storage at room temperature. These results were later confirmed by others, both in regard to bread^{22, 57, 59, 189} and starch pastes.²² In all cases, crumb firmness or 'fixed strain' techniques were employed for making the measurements.

Similar conclusions were reached by still others,^{40, 69} using crumb 'softness' tests, although simultaneous measurements with the Farinograph⁶⁹ indicated a slightly greater rate of decrease in the consistency of the crumb doughs when the adjunct was present.

Anti-firming effects have also been reported for certain mono- and di-glycerides^{22, 36, 38, 59, 201} as well as for several other commercial emulsifiers.^{22, 24, 59}

Polyoxyethylene monostearate compounds, varying in average degree of polymerisation of the polyoxyethylene radical from 4 to 20, as well as *n*-ethanol stearamide¹¹ and polyethylene glycol monolaurate⁵⁹ have a greater anti-firming effect at 0.5 per cent. concentration (flour basis) than similar levels of other adjuncts studied to date.^{22, 59, 189} Lesser effects have been noted for mono- and di-glycerides^{22, 59, 189} and a group of sorbitan derivatives.^{22, 59} In addition, Edlemann and Cathcart⁵⁹ have tested a series of surface active amines of relatively low molecular weight and their effectiveness in preventing the firmness change in bread varied from poor to good. Many of these compounds, however, had some deleterious effects which would discourage their use in bread.

In contrast to these findings, Sumner and Thompson¹⁹⁹ and Bradley²⁸ have reported that agents such as polyoxyethylene monostearate and the mono- and di-glycerides act as crumb softeners but do not retard the rate of staling. These workers,

however, based their conclusions on crumb softness measurements, the disadvantage of which have been pointed out earlier.

The profound effect of polyoxyethylene monostearate in retarding the firming of bread crumb upon ageing has aroused interest concerning its mode of action. Kass⁹⁸ has discussed this problem in a general theoretical manner. Unpublished data from several laboratories show that this reagent partially inhibits the gelatinisation and swelling of starch granules and, like the fatty acids, forms complexes with the amylose component of defatted, autoclaved starch pastes.* Since such experiments with defatted starch pastes have shown that polyoxyethylene monostearate has a strong affinity for amylose, the linear component, and little affinity for amylopectin, the branched component, the question arises whether its effect on the firmness of bread crumb may possibly be associated with the lower hydration of the starch leaving more water free to act as a plasticiser. Carson, Marnett and Selman⁴⁰ baked bread from doughs made with and without the addition of 0.5 per cent. polyoxyethylene monostearate and containing varying amounts of water. Even with about 10 per cent. extra water, the bread baked without the emulsifier was less compressible than that with no extra water but containing 0.5 per cent. of the emulsifier. Bread baked from doughs, to which 'Pentasol' and *n*-butanol, which are efficient amylose precipitants, were added, showed about the same rate of change in crumb compressibility with time of storage. They conclude that the action of polyoxyethylene monostearate in bread cannot be due solely to the availability of more water to serve as a plasticiser but that complex formation with amylose and amylopectin molecules protruding from the surface of the granules hinders the alignment and hydrogen bonding of starch chains, thus retarding the development of firmness of the crumb. Some doubt might be raised as to the significance of results obtained by baking bread containing Pentasol and *n*-butanol since it is questionable whether these alcohols would remain in the bread during baking. Also the bonding strength between the linear fraction and Pentasol is probably much weaker than with polyoxyethylene monostearate.

Recent investigations by Bice²² have indicated that in the concentrations effective in decreasing the rate of firming of bread crumb, polyoxyethylene monostearate acts principally by spreading on the surfaces of the starch granules, thereby inhibiting the formation of cohesive bonds between them. The adjunct had no effect on the gelatinisation temperature range of wheat starch

* See discussion by T. J. Schoch in Chapter 6, Vol. I.

as determined by loss of anisotropy. (For this experiment aqueous suspensions containing 1 per cent. wheat starch and 1 per cent. of the emulsifier were employed.) Measurements of granule size showed that a slight inhibition in the secondary swelling of the wheat starch granules occurred, but the effect was not considered great enough to explain the marked delay in the initial rise in Amylograph viscosity. Microscopic examination of the treated suspensions during pasting in the Amylograph indicated that great increases could occur in the size of the starch granules without any increase in viscosity being recorded. It, therefore, appeared that this emulsifier was acting principally to reduce the frictional forces between particles. Forty per cent pastes of defatted wheat starch to which 1 per cent. of polyoxyethylene monostearate (dry starch basis) was added after the paste had been cooled to 35° C. were indistinguishable in appearance and feel from similar pastes to which the adjunct had been added prior to gelatinisation. When added to 3 per cent. pastes of defatted wheat starch to give a concentration of 1 per cent. (dry starch basis), this emulsifier proved to be a rather poor fractionating agent. As undefatted wheat starch pastes, upon being autoclaved and cooled, spontaneously yield about 10 to 12 per cent. of the amylose as a crystalline complex with the naturally occurring lipids of the starch granule, the weak fractionating ability of polyoxyethylene monostearate would appear to be of little significance in bread or non-defatted starch pastes where more efficient fractionating agents are present. It is significant that stearic acid had no anti-firming effect in bread at 0.5 per cent. concentration (flour basis). Moreover, Bice found that 1 per cent. of polyoxyethylene monostearate delayed the firmness changes in 40 per cent. waxy starch (corn and sorghum) pastes which consist almost entirely of amylopectin.

The fact that polyoxyethylene monostearate has little influence on the swelling power change in starch pastes or bread at concentrations which markedly delay firming, in conjunction with other observations leads to the suggestion that the decrease in swelling power which occurs upon the storage of bread crumb may be due largely to changes occurring within the starch granule whereas the crumb firmness transformation is perhaps due to changes taking place both between and within granules. This adjunct appears to inhibit the change between granules, whereas the change within the granules would continue unretarded (due to lack of penetration of the adjunct). This would explain the gradual though delayed increase in firmness which occurs even in treated starch pastes and bread. These observations appear to

explain the contrary effects of polyoxyethylene monostearate on the changes in crumb compressibility and crumb swelling power with time.

Other heteropolar compounds which delay the rate of firming in bread may act in a similar manner. Carlin³⁷ states that mono-glycerides appear to influence the diameter and length of gluten strands, the gelatinisation or swelling properties of starch and the quantity of soluble starch found in baked bread.

Another recent technological advance in the United States which is pertinent to the staling problem is the introduction in November, 1949, of partly-baked rolls into the retail market.⁷⁶ The rolls are baked at reduced temperatures of about 275-300° F. for a sufficient length of time to gelatinize the starch and attain full volume and rigidity but without any semblance of crust colour. The rolls are only baked sufficiently to retain their shape and volume on cooling and to provide an ample safety factor in the thermal destruction of vegetative forms of pathogenic organisms. Time-temperature studies on rolls baked in a hearth oven at 275° F. showed that the internal temperature reaches 175° F. when proper rigidity is attained; the heat treatment is equivalent to 250 minutes at 150° F. which is eight to nine times that considered adequate to ensure the destruction of common disease organisms. After cooling, the rolls are packaged in moisture-proof cellophane bags, cellophane wrapped on hard-surfaced trays, or packed in cellophane-window boxes. Experience has indicated that rolls baked in this manner under sanitary conditions will remain mould-free for five days or more without refrigeration. For added protection against mould growth, mould inhibitors such as the propionates of sodium and calcium or sodium diacetate may be used. The purchaser completes the baking process by heating the partly-baked rolls for six to eight minutes at 425-450° F. While staling of the rolls occurs during storage, the completion of the baking process in the home just prior to consumption yields hot freshly-baked products.

Another method of altering the rate of firming of bread which has shown promise in laboratory studies involves the use of enzyme supplements in bread. Conn *et al.*⁵⁴ report that bread compressibility is increased by additions of both alpha-amylase and proteinase to the bread formula.

Recently, Cathcart *et al.*⁴⁹ have made the interesting observation that stale bread may be refreshed within the wrapper by heating to 140° F. by means of high frequency heat. Further, wrapped, sliced bread may be made sterile, with regard to moulds, by this process. The heat treatment did not decrease the thiamine content.

VIII. Suggestions for Future Research

Over a period of years, considerable technological research has been carried out in an effort to solve or alleviate the problem of bread staling. The effects of various adjuncts, variations in baking formula, baking procedure, and storage conditions have been rather extensively studied. As has been pointed out earlier in this chapter, conflicting results have frequently been obtained. These difficulties can be ascribed largely to the use of different methods for evaluating staleness and to a lack of agreement concerning the definition of staleness.

One of the prime requisites for future research is a clear-cut understanding of what constitutes staleness in a loaf of bread from the standpoint of consumer acceptability. There is a need for a precise statistical study designed to correlate the organoleptic evaluation of staling with physical and chemical tests. In making such a comparison, the data from those tests which tend to change in a curvilinear manner with time, must be subjected to special mathematical analysis. Those physical tests which are found to be highly correlated with the organoleptic scores would seem to be the most appropriate to use as measures of staling rate.

The soluble 'starch' extracted from bread by means of water at room temperature should be characterised more precisely, especially since the amount which can be extracted decreases during ageing of the bread. In addition, it would also be of interest to establish the molecular size of the total starch substance of bread to ascertain the extent of degradation which is brought about by amylases during the early stages of baking.

The mode of action of polyoxyethylene monostearate and similar compounds on bread, starch pastes and gluten should be investigated further. It might be anticipated that polyoxyethylene monostearate, because of its detergent properties, would have a peptising action on the gluten proteins.

In making ageing studies on starch pastes and bread, it is necessary to consider the possibility of changes occurring both within and between starch granules. Consequently, it would be of interest to investigate ageing changes which occur in a paste in which the granules have been completely destroyed. To prepare such a paste, it would probably be necessary to autoclave a dilute paste (about 3 per cent. concentration) for about two hours at 17-19 lb. gauge pressure, remove any remnants of granules by supercentrifugation and then concentrate the sol to some high value, 40 per cent. if possible.

It would be of interest to determine why the swelling power and Farinograph consistency values for 40 per cent. waxy starch

pastes increase during storage whereas these same values for bread and 40 per cent. wheat starch pastes decrease.²² At the same time, all of these systems become firmer with time. These results do not appear to be consistent with the assumption that the physical changes in bread are associated only with changes in the amylopectin component of the starch.

Solution of these problems should aid considerably in our understanding of bread staling-phenomena and could lay the groundwork for better commercial control of staling in the future.

REFERENCES

1. C. L. ALSBERG, *Ind. Eng. Chem.*, 1926, **18**, 190.
2. C. L. ALSBERG, *Cereal Chem.*, 1927, **4**, 485.
3. C. L. ALSBERG, from "A Comprehensive Survey of Starch Chemistry" edited by R. P. Walton. Chem. Catalog Co., pp. 87-99, 1928.
4. C. L. ALSBERG, *Wheat Studies of the Food Res. Inst.*, 1935, **11**, 229.
5. C. L. ALSBERG, *Wheat Studies of the Food Res. Inst.*, 12, 1936, **6**, 221.
6. C. L. ALSBERG and E. P. GRIFFING, *Cereal Chem.*, 1927, **4**, 411.
7. C. L. ALSBERG and E. E. PERRY, *Proc. Am. Soc. Biol. Chem.*; *J. Biol. Chem.*, 1925, **63**, 66. (Through C. A. 1925, **19**, 3612.)
8. C. L. ALSBERG and O. S. RASK, *Cereal Chem.*, 1924, **1**, 107.
9. American Association of Cereal Chemists. "Cereal Laboratory Methods." Am. Assoc. Cereal Chemists, University Farm, St. Paul, 5th ed., 1947.
10. C. A. ANKER and W. F. GEDDES, *Cereal Chem.*, 1944, **21**, 335.
11. H. L. BACHRACH and D. R. BRIGGS, *Cereal Chem.*, 1947, **24**, 492.
12. L. H. BAILEY, *Cereal Chem.*, 1930, **7**, 340.
13. L. H. BAILEY, *Cereal Chem.*, 1932, **9**, 65.
14. 'Bread in the Army', *Bakers' Digest*, 1941, **16**, 111.
15. *Bakers' Digest*, 1941, **15**, 197.
16. *Bakers' Review*, p. 29, September, 1940.
17. H. E. BARNARD and H. E. BISHOP, *Ind. Eng. Chem.*, 1914, **6**, 736.
18. F. L. BATES, D. FRENCH and R. E. RUNDLE, *J. Am. Chem. Soc.*, 1943, **65**, 142.
19. I. A. BERG, *Baking Tech.*, 1926, **5**, 205.
20. I. A. BERG, *Am. Soc. Bakery Eng. Bull.* 39, January, 1929.
21. I. A. BERG and C. B. MORISON, *Baking Tech.*, 1925, **4**, 83.
22. C. W. BICE, Ph.D. Dissertation, University of Minnesota, January, 1950.
23. C. W. BICE and W. F. GEDDES, *Cereal Chem.*, 1949, **26**, 440.
24. C. W. BICE and W. F. GEDDES, unpublished results, University of Minnesota.
25. R. M. BOHN, *Bakers' Helper*, 1944, **1022**, 40.
26. R. T. BOHN and H. H. FAVOR, *Cereal Chem.*, 1945, **22**, 296.
27. BOUSSINGAULT, *Ann. Chim. Phys.*, 1852, **36**, 490.
28. W. B. BRADLEY, *Bakers' Digest*, 1949, **23**, 5; see also Proc. 24th Annual Meeting Am. Soc. Bakery Engineers, 1948, 53.
29. SADIE BRENNER, S. G. DUNLOP, and V. O. WODICKA, *Cereal Chem.*, 1948, **25**, 367.
30. British Baker, *Brit. Baker*, p. 24, April, 1935.
31. W. E. BROEG, *Bakers' Helper*, 1937, **68**, 56.
32. R. W. BROOKS, Proc. 4th Annual Meeting Am. Soc. Bakery Engineers, p. 173, 1927.
33. S. W. BUTTERWORTH and W. J. COLBECK, *Cereal Chem.*, 1938, **15**, 475.
34. G. V. CAESAR, 'Starch and the hydrogen bond' from "Starch and Its Derivatives" by J. A. Radley, Chapman & Hall, Ltd., London, pp. 121-127, 1943.

35. G. V. CAESAR, 'The hydrogen bond in starch as a basis for interpreting its behavior and reactivity' from "*Chemistry and Industry of Starch*" by R. W. Kerr, Academic Press, Inc., Publishers, New York, pp. 178-187, 1944.
36. G. T. CARLIN, presented at 34th Annual Meeting, Am. Assoc. Cereal Chem., New York, 1949.
37. G. T. CARLIN, presented at 34th Annual Meeting, Am. Assoc. Cereal Chem., New York, 1949.
38. G. T. CARLIN, R. P. HOPPER and M. J. THOMAS, presented at 32nd Annual Meeting, Am. Assoc. Cereal Chem., Kansas City, 1947.
39. J. J. CARNAUD and F. DE BASSEINDRE, *Brit.* 396, 634, March 2nd, 1933; *Fr.* (unknown), November 2nd, 1932. (Through *Brit. Chem. Abstracts B*, 1933, p. 890.)
40. B. G. CARSON, L. F. MARNETT and R. W. SELMAN, *Cereal Chem.*, 1950, **27**, 438.
41. W. H. CATHCART, *Food Industries*, 1939, **11**, 68, 109, 200, 233.
42. W. H. CATHCART, *Cereal Chem.*, 1940, **17**, 100.
43. W. H. CATHCART, *Cereal Chem.*, 1941, **18**, 771.
44. W. H. CATHCART, *Bakers' Digest*, 1941, **15**, 201.
45. W. H. CATHCART, *Bakers' Digest*, 1944, **18**, 39.
46. W. H. CATHCART and S. V. LUBER, *Ice and Refrig.*, 1938, **95**, 212.
47. W. H. CATHCART and S. V. LUBER, *Ind. Eng. Chem.*, 1939, **31**, 362.
48. W. H. CATHCART and S. V. LUBER, *Cereal Chem.*, 1939, **16**, 430.
49. W. H. CATHCART, J. J. PARKER and H. G. BEATTIE, *Food Technology*, 1947, **1**, 174.
50. Chicago Quartermaster Depot. Progress reports on canned bread. August 5th, 1944-July, 1945.
51. K. N. CHISHOVA, *Akad. Nauk. S.S.S.R., Inst. Biokhim., Biokhimisya Khlebopecheniya, Sbornik*, 1942, , **3**, 131 (in English, 139). (Through *C. A.* 1943, **37**, 5500.)
52. K. A. CLENDENNING, *Can. J. Research B*, 1945, **23**, 239.
53. Y. F. COMBS, *Cereal Chem.*, 1944, **21**, 319.
54. J. F. CONN, J. A. JOHNSON and B. S. MILLER, *Cereal Chem.*, 1950, **27**, 191.
55. L. B. COOK, *Bakers' Digest*, 1944, **18**, 122.
56. M. D. COULTER, U.S. 2,193,622, March 12th, 1940. (Through *C. A.* 1940, **34**, 4830.)
57. L. B. CROSSLAND and H. H. FAVOR, *Cereal Chem.* 1949, **26**, 15.
58. J. S. DAVIS and W. ELDRED, *Food Research Inst. Pub.* 1923, **1**, 71.
59. E. C. EDELMANN and W. H. CATHCART, *Cereal Chem.*, 1949, **26**, 345.
60. A. K. EPSTEIN and B. R. HARRIS, U.S. 2,009,440, July 30th, 1935. (Through *C. A.* 1935, **29**, 6322.)
61. A. K. EPSTEIN and B. R. HARRIS, U.S. 2,040,249, May 12th, 1936. (Through *C. A.* 1936, **30**, 4584.)
62. N. C. ESSELBOUGH, Ohio State University, *Abs. Doctoral Diss.*, 1944, **44**, 165. (Through *Expt. Sta. Rec.*, 1945, **93**, 219.)
63. H. H. FAVOR and L. B. CROSSLAND, Reports 1, 2 and 3 by R. T. Vanderbilt Co., Inc., to the Committee on Food Research, Quartermaster Food and Container Institute for the Armed Forces, Chicago, October 1st, 1946, to June 30th, 1947.
64. H. H. FAVOR and N. F. JOHNSTON, *Cereal Chem.*, 1947, **24**, 346.
65. H. H. FAVOR and N. F. JOHNSTON, *Cereal Chem.*, 1948, **25**, 424.
66. E. A. FISHER, Research Assoc. of Brit. Flour Millers' Spec. Rept. No. 11, 1934.
67. E. A. FISHER, P. HALTON and R. H. CARTER, *Cereal Chem.*, 1937, **14**, 135.
68. A. L. FOLEY, "*College Physics*," 2nd ed., P. Blakiston's Son and Co., Inc., Philadelphia, 777 pp., 1937.
69. J. FREILICH, *Cereal Chem.*, 1948, **24**, 87.
70. C. H. F. FULLER, *J. Soc. Chem. Ind.*, 1938, **57**, 562.
71. G. GARNATZ and E. G. KORNREICH, Proc. 19th Annual Meeting Am. Soc. Bakery Engineers, p. 40, 1942.
72. W. F. GEDDES, 'Baking practices and trends in Scotland' from *Observa-*

tions on Milling and Baking Practices in England and Scotland, Board of Grain Commissioners, Grain Research Lab. Dept. of Trade and Commerce, Canada, October 13th, 1936, pp. 12-15.

73. W. F. GEDDES, H. L. BACHRACH, D. R. BRIGGS, L. EVANS, P. P. NOZNICK and D. E. SMITH, Reports 2 and 3 by University of Minnesota to the Committee on Food Research, Office of Quartermaster General, November 1st, 1945, to January 15th, 1946, and August 1st, 1945.
74. W. F. GEDDES, R. A. BOTTOMLEY, C. W. BICE and R. STENBERG, Report No. 10 (C-300) by the University of Minnesota to the Committee on Food Research, Quartermaster Food and Container Institute for the Armed Forces, Chicago, March 1st to June 30th, 1949.
75. W. F. GEDDES, C. W. BRABENDER and R. A. BOTTOMLEY, presented at the 34th Annual Meeting. Am. Assoc. Cereal Chem., New York (1949).
76. General Mills presents a revolutionary new baking technique, Brown 'n Serve Rolls. General Mills, Inc., Products Control Department, General Mills, Inc., Minneapolis, Minnesota, 20 pp., 1949.
77. C. A. GLABAU, *Bakers' Weekly*, 1938, 100, 3, 35.
78. C. A. GLABAU and P. F. GOLDMAN, *Cereal Chem.*, 1938, 15, 541.
79. G. A. GRANT, J. B. MARSHALL and W. H. WHITE, *Can. J. Research, F*, 1945, 23, 123. (Through *Bakers' Digest*, 1945, 19, 83.)
80. R. A. GORTNER, *Cereal Chem.*, 1933, 10, 298.
81. F. H. HAFNER, *Bakers' Digest*, 1942, 16, 282.
82. R. H. HARRIS and L. D. SIBBITT, *Cereal Chem.*, 1941, 18, 585.
83. W. Z. HASSID, *Wallerstein Lab. Commun.*, 1945, 8, 34.
84. *Handbook of Chemistry and Physics*, 28th ed., p. 2227, Chemical Rubber Publishing Co., Cleveland, 1944.
85. W. L. HEALD, *Cereal Chem.*, 1937, 14, 481.
86. G. E. HILBERT and MAJEL M. MACMASTERS, *J. Biol. Chem.*, 1946, 162, 229.
87. R. M. HIXON, *Bakers' Digest*, 1943, 17, 19.
88. R. M. HIXON and G. F. SPRAGUE, *Ind. Eng. Chem.*, 1942, 34, 959.
89. P. HOLTON, from a lecture before the Midwest Section, A.A.C.C. News Letter, American Association of Cereal Chemists No. 67, pp. 8-9, May, 1946. See also T. SOLOSKI and J. CRYNS, *Transactions Am. Assoc. Cereal Chemists*, 1950, 8, 107.
90. J. P. HUTCHINSON, Res. Assoc. of Brit. Flour Millers, Special Report No. 15, pp. 1-27, 1936.
91. ALLENE JEANES, N. C. SCHIELTZ and C. A. WILHAM, *J. Biol. Chem.*, 1948, 176, (2)617.
92. L. KARACSONYI, *Z. Untersuch. Lebensm.*, 1928, 56, 479. (Through C. A. 1929, 23, 3029.)
93. L. KARACSONYI, *Z. Untersuch. Lebensm.*, 1929, 58, 517. (Through C. A. 1930, 24, 1905.)
94. L. KARACSONYI, *Cereal Chem.*, 1929, 6, 241.
95. L. KARACSONYI, *Mexogazdasagi Kutatasek*, 1930, 3, 192. (Through C. A. 1931, 25, 2774.)
96. L. KARACSONYI, *M. Chem. Folyoirat.*, 1930, 36, 59. (Through C. A. 1931, 25, 2491.)
97. L. KARACSONYI and C. H. BAILEY, *Cereal Chem.*, 1931, 8, 44.
98. J. P. KASS, presented at 34th Annual Meeting, Am. Assoc. Cereal Chem., New York (1949).
99. J. R. KATZ, *Holl.* 1,816 (no date). (Through C. A. 1914, 8, 2204.)
100. J. R. KATZ, *Chem. Weekblad.*, 1912, 9, 1023. (Through C. A. 1913, 7, 2073.)
101. J. R. KATZ, *Pharm. Weekblad.*, 1912, 49, 1183; *Chem. Weekblad.*, 1912, 9, 1023. (Through E.S.R. 1913, 28, 861.)
102. J. R. KATZ, *Pharm. Weekblad.*, 49, 618; also in *Z. Electrochem.*, 1913, 19, 202. (Through C. A. 1912, 6, 2658.)
103. J. R. KATZ, *Chem. Weekblad.*, 1913, 10, 489. (Through C. A. 1913, 7, 3169.)
104. J. R. KATZ, *Verslag. Akad. Wetenschappen*, 1914, 23, 655. (Through C. A. 1915, 9, 1808.)

105. J. R. KATZ, *Brit.* 5, 154, Feb. 27th, 1914. (Through *C. A.* 1915, 9, 2275.)
106. J. R. KATZ, *Verslag. Akad. Wetenschappen*, 1914, 23, 652. (Through *C. A.* 1915, 9, 1808.)
107. J. R. KATZ, *Z. physiol. Chem.* 1915, 95, 104, 136, 147. (Through *C. A.* 1916, 10, 943.)
108. J. R. KATZ, *Z. physiol. Chem.*, 1916, 96, 314.
109. J. R. KATZ, *Chem. Weekblad.*, 1921, 18, 317.
110. J. R. KATZ, "A Comprehensive Survey of Starch Chemistry" edited by R. P. Walton. The Chem. Catalog Co., pp. 100-117, 1928.
111. J. R. KATZ, *Z. physik. Chem. A.* 1930, 150, 37. (Through *C. A.* 1931, 25, 16.)
112. J. R. KATZ, *Z. physik. Chem.*, A. 1932, 158, 346. (Through *C. A.* 1932, 26, 3425.)
113. J. R. KATZ, *Bakers' Weekly*, 1934, July 21st, 36.
114. J. R. KATZ, *Bakers' Weekly*, 1934, 82, 31. (Through *C. A.* 1935, 29, 3409.)
115. J. R. KATZ, *Bakers' Weekly*, 1934, 83, 26. (Through *C. A.* 1935, 29, 3411.)
116. J. R. KATZ, *Bakers' Weekly*, 1934, 84, 25. (Through *C. A.* 1935, 29, 3411.)
117. J. R. KATZ, *Bakers' Weekly*, 1934, March 24th, 34.
118. J. R. KATZ, *Bakers' Weekly*, 1934, 82, 40; 1934, 82, 36. (Through *C. A.* 1935, 29, 3410.)
119. J. R. KATZ, *Z. physik. Chem.*, A. 1934, 169, 321. (Through *C. A.* 1934, 28, 6860.)
120. J. R. KATZ, *Z. physik. Chem. A.*, 1934, 170, 421. (Through *C. A.* 1935, 29, 1169.)
121. J. R. KATZ, *Z. physik. Chem. A.*, 1934, 170, 430.
122. J. R. KATZ, *Bakers' Weekly*, 1934, 82, 40. (Through *C. A.* 1935, 29, 3410.)
123. J. R. KATZ, *Bakers' Weekly*, 1934, 84, 31. (Through *C. A.* 1935, 29, 3410.)
124. J. R. KATZ, *Bakers' Weekly*, 1935, July 13th, 87, 26.
125. J. R. KATZ, *Bakers' Weekly*, 1935, 85, 37. (Through *C. A.* 1935, 29, 3410.)
126. J. R. KATZ and J. C. DERKSEN, *Z. physik. Chem. A.*, 1933, 167, 129. (Through *C. A.* 1934, 28, 1784.)
127. J. R. KATZ and TH. B. v. ITALLIE, *Z. physik. Chem. A.*, 1930, 150, 90. (Through *C. A.* 1931, 25, 16.)
128. J. P. KATZ and TH. B. v. ITALLIE, *Z. physik. Chem. A.*, 1931, 155, 199. (Through *C. A.* 1932, 26, 2910.)
129. J. R. KATZ and L. M. RIENTEMA, *Z. physik. Chem. A.*, 1930, 150, 67. (Through *C. A.* 1931, 25, 16.)
130. J. R. KATZ and A. WEIDINGER, *J. physik. Chem. A.*, 1934, 169, 339. (Through *C. A.* 1934, 28, 6860.)
131. J. R. KATZ and A. WEIDINGER, *Z. physik. Chem. A.*, 1935, 171, 181. (Through *C. A.* 1935, 29, 2247.)
132. J. R. KATZ and A. WEIDINGER, *Z. physik. Chem. A.*, 1937, 180, 423. (Through *C. A.* 1938, 32, 2773.)
133. R. W. KERR, "Chemistry and Industry of Starch," Academic Press, Inc., New York, pp. 382-391, 1944.
134. R. W. KERR, an informal discussion given at the Starch Symposium held at Nippersink, Wisconsin, Sept. 10th-13th, 1945.
135. A. A. KHRUSTALEV and N. N. MUSERSKII, *Voprosui Pitaniya*, 1935, 4, 70. (Through *C. A.* 1936, 30, 6069.)
136. A. G. KUHLMANN and O. N. GOLOSISOVA, *Cereal Chem.*, 1936, 13, 202.
137. A. G. KUHLMANN and E. P. BALASHEVA, *Gosudarst. Nauch.-Issledovatel. Inst. Kolloid. Khim. Teknol. Protsessy i Kontrol Pishchevei. Ind.* 1938, 175.
138. L. H. LAMPITT, C. H. F. FULLER and N. GOLDENBERG, *J. Soc. Chem. Ind.*, 1941, 60, 301.
139. S. LANGENDORF, *Bakers' Helper*, 1942, 78, 975.
140. G. LEFFINGWELL and M. A. LESSER, *Bakers' Digest*, 1944, 18, 118.
141. G. LEFFINGWELL and M. A. LESSER, *Bakers' Helper*, 1945, 83, 1042.
142. M. M. MACMASTERS, C. W. BICE and G. E. HUBERT. Presented before Am. Assoc. Cereal Chem., Niagara Falls (1946).

143. M. M. MACMASTERS, G. E. HILBERT, M. J. COX., J. W. ECK and C. W. BICE. Presented before Am. Assoc. Cereal Chem., Niagara Falls (1946).
144. M. MAGRUDER, United Press Dispatch St. Paul Pioneer Press, April 22nd, 1946.
145. J. G. MALLOCH, *Can. J. Research*, 1929, **1**, 110.
146. C. E. MANGELS, *Cereal Chem.*, 1934, **11**, 86.
147. C. E. MANGELS, *Cereal Chem.*, 1934, **11**, 571.
148. C. E. MANGELS and C. H. BAILEY, *J. Am. Chem. Soc.*, 1933, **55**, 1981.
149. C. E. MANGELS and C. H. BAILEY, *Ind. Eng. Chem.*, 1933, **25**, 456.
150. G. W. MARTIN, *Food*, 1944, **13**, 129. (Through *C. A.* 1944, **38**, 4045.) (Through *Bakers' Digest*, 1944, **18**, 128.)
151. J. MASSON, *Bread Belg.* 438, 517, March 30th, 1940. (Through *C. A.* 1942, **36**, 2950.)
152. K. H. MEYER, W. BRENTANO and P. BERNFELD, *Helv. Chim. Acta*, 1940, **23**, 845.
153. Millers' National Federation Technical Committee. *Bakers' Digest*, 1941, **16**, 42.
154. T. MORAN, Correspondence from Ministry of Food, Cereals Research Station, Old London Road, St. Albans, Hertfordshire, England. (Aug. 20th, 1945.)
155. M. P. NEUMANN, *Z. ges. Getreidew.*, 1914, **6**, 119. (Through *C. A.*, 1915, **9**, 2554.)
156. J. P. NIELSEN and PEGGY C. GLEASON, *Ind. Eng. Chem. (Anal. Ed.)*, 1945, **17**, 131.
157. B. A. NIKOLAYEV, *Cereal Chem.*, 1941, **18**, 790.
158. P. P. NOZNICK and W. F. GEDDES, *Cereal Chem.*, 1943, **20**, 463.
159. P. P. NOZNICK, P. P. MERRITT and W. F. GEDDES, *Cereal Chem.*, 1946, **23**, 297.
160. H. J. ONNES, *Food Industries*, 1937, **9**, 584.
161. E. OTT, U.S.P. 2,152,602, March 28th, 1939. (Through *C. A.* 1939, **33**, 5085.)
162. P. PELSSENKE, *Bakers' Tech. Digest*, 1938, **12**, 197.
163. P. G. PIRRIE, *Bakers' Weekly*, 1940, **108**, 4: 37.
164. W. PLATT, *Cereal Chem.*, 1930, **7**, 1.
165. W. PLATT and R. POWERS, *Cereal Chem.*, 1940, **17**, 601.
166. D. B. PRATT, Jr., *Bakers' Digest*, 1944, **18**, 40.
167. L. H. PULKKI, *Cereal Chem.*, 1938, **15**, 749.
168. J. A. RADLEY, "Starch and Its Derivatives," Chapman & Hall, Ltd., London, pp. 110-115, 1943.
169. O. S. RASK and C. L. ALSBERG, *Cereal Chem.*, 1924, **1**, 7.
170. H. C. REITZ, Ph.D. thesis, University of Minnesota, June, 1938, pp. 1-157.
171. Reports supplied by Standard Brands, Inc.
172. A. ROTSCH, *Jahresber. Inst. Backerei Reichsanst. Getreideverarb.* 1940, **6**, 59. *Chem. Zentr.*, 1941, **1**, 3159. (Through *C. A.* 1943, **37**, 6750.)
173. L. SAIR and W. R. FETZER, *Ind. Eng. Chem.*, 1944, **36**, 205.
174. M. SAMEC and J. R. KATZ, *Z. physik. Chem.*, 1937, **180**, 436. (Through *C.A.* 1938, **32**, 2773.)
175. M. SAMEC, J. R. KATZ and R. KLEMEN, *Z. physik. Chem.*, 1933, **163**, 291. (Through *C. A.* 1933, **27**, 2840.)
176. R. M. SANDSTEDT, C. E. JOLITZ and M. J. BLISH, *Cereal Chem.*, 1939, **16**, 780.
177. T. J. SCHOCH, 'The Fractionation of Starch' from "Advances in Carbohydrate Chemistry," Vol. I, edited by W. W. Pigman and M. L. Wolfram, Academic Press, Inc., New York, pp. 247-277, 1945.
178. T. J. SCHOCH, *Cereal Chem.*, 1941, **18**, 121.
179. T. J. SCHOCH, *J. Am. Chem. Soc.*, 1942, **64**, 2957.
180. T. J. SCHOCH and D. FRENCH, *Cereal Chem.*, 1949, **24**, 231.
181. T. J. SCHOCH and D. FRENCH, Reports 1, 2, 3, 4 and 5 by Corn Products Refining Co. to Committee on Food Research, Office of the Quarter-

- master General, June 4th, 1945, June 20th, 1945, June-July, 1945, August, September and October, 1945, and August 1st to December 31st, 1945.
182. T. J. SCHOCH and C. B. WILLIAMS, *J. Am. Chem. Soc.*, 1944, **66**, 1232.
 183. F. D. SCHOONOVER, *Am. Soc. Bakery Eng. Bull. No. 132*, July, 1945.
 184. A. S. SCHULTZ and Q. LANDIS, *Cereal Chem.*, 1932, **9**, 305.
 185. C. SCHWEIZER, *Mitt. Lebensm. Hyg.*, 1930, **21**, 1. (Through *C. A.* 1930, **24**, 3288.)
 186. R. W. SELMAN, Kansas City, Mo., private communication (1944).
 187. W. G. SHRENK, A. C. ANDREWS and H. H. KING, *Ind. Eng. Chem.*, 1947, **39**, 113.
 188. ELSIE SINGRUEN, *Milling Production*, 1946, **11**, 10.
 189. O. SKOVHOLT and R. L. DOWDLE, *Cereal Chem.*, 1950, **27**, 26.
 190. Société pour l'étude des procédés de conservation du pain. Fr. 842,122, June 6th, 1939. (Through *C. A.* 1940, **34**, 4829.)
 191. O. E. STAMBERG and C. H. BAILEY, *Cereal Chem.*, 1939, **16**, 309.
 192. O. E. STAMBERG and C. H. BAILEY, *Cereal Chem.*, 1939, **16**, 319.
 193. O. E. STAMBERG and C. H. BAILEY, *Cereal Chem.*, 1939, **16**, 330.
 194. O. E. STAMBERG and C. H. BAILEY, *Bakers' Helper*, 1939, **71**, 1104.
 195. STEIN HALL CO., C. F. YAEGER, 1932.
 196. W. R. STELLER and C. H. BAILEY, *Cereal Chem.*, 1938, **15**, 391.
 197. W. L. STOCKHAM, *No. Dak. Agr. Expt. Sta. Bull.*, 1917, **120**, 97. (Through *C. A.* 1917, **11**, 3064.)
 198. J. STRAUB and P. HIRSCH, *Chem. Weekblad.*, 1935, **32**, 120.
 199. R. J. SUMNER and J. B. THOMPSON, presented at 33rd Annual Meeting, Am. Assoc. Cereal Chem., May 23rd, 1948, Cincinnati.
 200. W. A. TAYLOR (to Atlas Powder Co.) U.S.P. 2,285,065, June 2nd, 1942. (Through *C. A.* 1942, **36**, 6694.)
 201. M. J. THOMAS, Proc. 23rd Annual Meeting Am. Soc. Bakery Engineers, pp. 33-40 (1947).
 202. L. G. TREMPER, *Bakers' Digest*, 1944, **18**, 23.
 203. CORNELIA TYLER and L. C. CARTWRIGHT, Report No. II to Atlas Powder Company, Foster D. Snell, Inc., New York, 1948.
 204. Unpublished work. Northern Regional Research Laboratory, Peoria, Ill.
 205. E. VERSCHAFFELT, *Pharm. Weekblad.*, 1912, **49**, 631; 1912, **52**, 1218. (Through *C. A.* 1912, **6**, 3295. *E. S. R.* 30, 859.)
 206. E. VERSCHAFFELT, *Chem. Weekblad.*, 1912, **9**, 544. (Through *C. A.* 1912, **6**, 3295.)
 207. A. S. WAHL, U.S.P. 1,155,530, October 5th, 1915. (Through *C. A.* 1915, **9**, 3309.)
 208. R. C. WANDS and D. R. BRIGGS, Div. Agric. and Biochem. Univ. Minnesota, St. Paul, Minn., Private Comm., 1950.
 209. R. L. WHISTLER, Report No. 10 (December 1st, 1946- June 30th, 1949) to Quartermaster Food and Container Institute for the Armed Forces, Chicago, Ill.
 210. R. L. WHISTLER and G. E. HILBERT, *J. Am. Chem. Soc.*, 1945, **67**, 1161.
 211. R. L. WHISTLER, S. A. WATSON and G. E. HILBERT, private communication from Northern Regional Research Laboratory, Peoria, Illinois, July 10th, 1946.
 212. R. WHYMPER, *Bakers' Helper*, 1945, **81**, 66.
 213. E. J. WILSON, Jr., T. J. SCHOCH and C. S. HUDSON, *J. Am. Chem. Soc.*, 1943, **65**, 1380.
 214. E. WOLSHANSKY, Austrian 148,831, March 3rd, 1937.
 215. SYBIL WOODRUFF and MAJEL M. MACMASTERS, *Univ. of Ill. Agr. Expt. Sta. Bull.* 445, pp. 43, August, 1938.

CHAPTER II

THE PAPER INDUSTRY

FUNDAMENTALLY, the manufacture of paper consists in beating cellulosic fibres in a water suspension to a state of division suitable for deposition as a thin 'web' or layer, to be subsequently dried. The various means of producing the correct 'stock' from the different forms of cellulose used commercially will not be considered here, as we are only concerned with the role of starch in the paper-making process.

The sheets or web produced in the process mentioned are very water-absorbent, often possessing little strength, and the sole outlet for such paper is its use as the well-known blotting-paper. By the addition of resin and alum a sized paper is produced that finds extensive application in printing or writing papers. For these purposes a fairly high tensile strength is required, the most important factor being the surface, which must not readily 'wet out,' so that written or printed impressions appear sharp and legible and spread only in a direction normal to the surface of the paper. The surface of a writing-paper should allow the pen to travel smoothly; and to obtain a whiter and smoother surface, clay and other filling materials are used to close the interstices between the fibres. These spaces may also be partly closed by manipulation of the paper stock on the machine. An extension of this method involves the use of starch, glue, casein, or some other film-forming colloid, which is capable of rendering the fibres more water-resistant and assisting in the production of a so-called sized paper.

The use of these colloids as auxiliary sizing agents increases the tensile strength and stiffness of the paper by bonding the fibres together, holds down small fibres, or corrects the elasticity of the individual fibre, as understood in the paper trade, which would otherwise project from the surface. They also increase the imperviousness, impart a crackle to the finished sheet and make it more resistant to abrasion and folding.

When the sizing agents are added to the beater, the paper is known as 'Beater', 'Engine' or 'Pulp' sized, or the finished web may be given a coating of size, a process known as 'Tub' sizing.

Engine Sizing.—Resin is largely used in sizing papers, but its high prices in recent years have naturally directed attention to cheaper substitutes, and the use of water-glass (sodium silicate) in the pulp, followed by the addition of alum, was found to give a gelatinous precipitate which on drying was found useful in the sizing. It could thus be used to replace a part of the resin normally employed. In passing, it may be noted that by the use of resin a porous paper may be produced which is, however, also suitable for writing on as the individual fibres are water-repellent, whereas a non-porous 'coated' paper is obtained by spreading on a medium of starch or glue together with mineral matter, e.g. china clay. The sizing material used must be colloiddally dispersed so that it can form a link between individual fibres and the bond so formed should be strong. Degradation of organic colloids to lower molecular weight particles often leads to water solubility and loss of adhesive strength. Starch appears capable of fulfilling the role of the ideal sizing agent providing all these factors are borne in mind. In practice these factors often militate one against the other and a balance must be struck between the values of the various properties. The adjustment of this balance has led to the appearance of many 'treated' starches on the market and the development of various techniques in the factory. Raw starch added to the beaters is not colloiddally dispersed and so fails in two of the desired characteristics for unless gelatinised or dispersed it cannot act as an adhesive. Although the raw starch retained in the web may gelatinise when the latter passes over the drying drums the retention of starch (1-3 per cent.) by the web at the 'wire' is only about 30 per cent. and this starch is very poorly dispersed throughout the paper. At the site of each granule there is an excessive amount of size for the job to be done (i.e. binding adjacent fibres where they are in contact) and in neighbouring spots there is insufficient or no fibre-binding agent. Various starches have different gelatinisation temperatures (see p. 314) and various granules of the same starch also vary in this respect, so that the heat and water present at the drying rolls may be sufficient to gelatinise only a fraction of the starch actually retained. This latter difficulty is overcome by the use of oxidised starches which have much lower gelatinisation temperatures than the corresponding raw starches. As they give mobile solutions, or dispersions, when heated with water, they therefore spread out on adjacent fibres when heated at the drying drums. In contrast to acid-modified starches oxidised starches do not significantly alter in efficiency with degree of oxidation, except in the ink resistance test.

Cobb and his co-workers^{7,8} found that when starch alone was used it slowed down sheet-formation and reduced the percentage solids present in the sheet after wet pressing, but in most cases increased the percentage of solids in the dry sheet. The comparatively high specific gravity and high water-holding power of starch account for these observations. The high water-holding power of starch also tends to increase the contraction of the starch on drying, but widely differing effects can be obtained by altering the water-holding properties of the starch. An ordinary starch, for example, swells and holds a very much greater amount of water than a 'soluble' or oxidised starch, thus causing a much greater contraction on drying; and when present in paper the unmodified starch paste gives a greater contraction of the sheet than a thin-boiling starch. It may in this case bring about a greater increase in sheet strength, but should it contract to a greater apparent volume than an equal quantity of thin-boiling starch, it would not be present as a continuous film but as a honeycomb structure containing air. In that case the sheet would not contract so much, and this drawback, together with the honeycomb structure, would weaken the strength as compared with a thin-boiling starch.

It has also been shown that the strength of a sheet containing an increased amount of starch passes through a maximum, an observation which confirms the well-known fact that starch is a poorer sheet-forming material than cellulose. Its action is similar to that of glues, which give a joint stronger than the glue itself (see chapter on Adhesives).

A further development of the use of sodium silicate for sizing is due to H. Wredé¹ and termed 'mineral starch sizing'. Equal weights of sodium silicate and starch are heated together until the starch has gelatinised, care being taken not to boil the mixture, which would result in a lowering of the viscosity of the solution (see Vol. I). This paste is added to the stock in the beater and when homogeneously distributed, alum is added to produce a precipitate.

According to Wredé, this method is very efficient for sizing papers intended for printing, and may be employed advantageously for certain writing papers for which the use of sodium silicate and starch in the ratio of 1 to 4 is recommended. For printing papers, about 3.5-5.0 per cent. of starch, calculated on the dry weight of the pulp, is used, and if the final reaction after precipitating with aluminium sulphate is acid, a loss of 30-40 per cent. of the starch may occur. E. Fues, however, obtains practically quantitative precipitation of the starch by adding the

aluminium sulphate in amount sufficient to give a final neutral reaction.

A. Lutz³ in his work found that if raw starch is added to the beater, 73·2 per cent. of it is retained by the paper, whereas with starch paste only 46·2 is retained. Blasweiler² has examined the mineral-starch-sizing of paper and compared the values obtained for strength, texture, etc., with those given by other methods of sizing. He concludes that this method gives a greater tensile strength as compared with raw starch, although the values shown by the latter are already high. The tensile strength of paper sized by this method is 27 per cent. greater than that obtained with an alkali-starch mixture containing equivalent amounts of starch and alkali. With loadings, the use of the mineral-starch size gave an increase of 15 per cent. on the amount of china clay retained, and an increase of 12 per cent. for talc, when compared with the use of starch alone. To obtain the best retention of loading agents, each particle of them should be coated with adhesive mixture, as a strong continuous film of adhesive gives the highest tensile strength to the paper, and if each particle has its own coating it stands a better chance of being retained when it comes into contact with a fibre. The starch 'mix' should therefore be added in two portions, one to the stock and one to the filler, before putting into the stock. If the filler is put in the beater with the raw starch, the loss of the latter often exceeds 50 per cent., depending on the amount of clay present and the 'freeness' of the sheet, because mechanical enmeshment of the particles is the only means of preventing loss, no adhesive forces coming into play when fibre, clay, and raw starch make contact.⁴

It will have been noticed that more starch is retained by the paper if raw starch is added to the beater than when it is first cooked to a paste with water.

This is due to two causes, the first being that on gelatinisation some of the starch goes into solution and will pass away with the back water. The vesicles of the swollen starch are fragile and readily broken down by the action of the beater to such particle size that is lost at the 'wire'.²⁷ As has already been discussed (Vol. I) starches vary in the ease with which the empty sacs can be disintegrated and the non-cereal starches, in particular, are readily reduced to such small dimensional particles that a great deal is lost at the 'wire'. Thus the addition of pre-gelatinised starch to the beater takes on the finer points of an art in assessing the degree of cooking required and the effect of such factors as the type of starch, pH of the water used, variation between different batches of the same variety of starch, operation of the beaters, etc.

To overcome this difficulty Rowland²⁸ stabilises the starch to mechanical operations through toughening the granules by gelatinising in the presence of formaldehyde and acetic acid. Another procedure is to modify the starch with formaldehyde and then disperse the formaldehyde-starch in sodium hydroxide and add to the beaters. The addition of an acidic compound, e.g. alum to the fibre suspension precipitates the starch complex. The pre-cooking of starch is open to one other objection by large mills and that is that an additional process is introduced into paper manufacture. This has led to the introduction by starch makers of a precooked, redried starch which disperses or swells in water for use by paper makers. An example of this type of product is Amijel.

The fundamentals of the processes involving precipitating dispersed starch have been discussed by A. M. Heald²⁹ and B. W. Rowland,²⁸ and C. C. Kesler and W. C. Black³⁰ have suggested alumina and fatty acids or soaps, respectively, as starch precipitants. The last workers find that soaps or fatty acids appear to form a complex with starch, raising the gelatinisation temperature and increasing the viscosity of the solutions when insoluble-soap-forming metallic ions, e.g. calcium ions are added to such solutions an insoluble precipitate of the hydrophobic soap and starch is precipitated.

The reaction between starch and soap was first described by Richard and Waite in 1933. They found that soaps behave towards sago pastes like mild alkalis which first lower the viscosity, but cause a rapid rise in the viscosity with further addition. They observed a minimum in a 5 per cent. paste at a soap concentration of about 0.15 per cent. on the weight of the starch. With stearate the initial fall is less and the subsequent rise more rapid than with oleate. In 2 per cent. farina pastes, the viscosity continues to fall, with the further addition of soap, with no indication of a subsequent rise. The effect, apparently is not due to the increased alkalinity alone, but is ascribed to a specific action between starch and soap.

In 1939 L. Lehrman suggested that fatty acid soaps can be absorbed by starches, and to investigate this theory and also the work of Richards and Waite further, Heald examined the behaviour of 0.5 per cent. tapioca starch solutions and numerous other starches towards a wide variety of soaps.

He confirmed that the various phenomena must be attributed to a specific colloidal interaction between starch and soap. When sodium oleate is added to a starch dispersion, the negative oleate ions are probably adsorbed by the starch particles. As the first

soap chains attached themselves to the starch particles, they may tend to lower the viscosity of the starch dispersion by displacing water of hydration from the surface of the particles and reducing their volume. Thus, there is a minimum in viscosity when about 1·5 per cent. soap is added on the weight of the starch. As more oleate ions are adsorbed with further additions of soap, the negative charge on the starch particles increases. At the same time, the viscosity increases in dispersions of 0·2 per cent. or more concentration, due probably to cohesive forces between the soap chains adsorbed on adjacent starch particles. When approximately 12 per cent. soap has been added in the case of most systems, there arises a condition of maximum viscosity, turbidity, and charge on the particles, and minimum hydration of the starch particles.

The increase in viscosity of a starch sol with the addition of soap is directly proportional to the chain length of the soap. Unsaturation in the soap chain tends to decrease the viscosity rise. The increase in viscosity is related to the amylopectin fraction dispersed in the sol, but also depends on the degree of solvation of the amylopectin. Centrifugal fractionation lowers the viscosity effect, whereas a dispersion of starch in formamide shows no viscosity increase with soap additions. Modification of the starch by enzymes or oxidising agents lowers the viscosity effect. The reaction of soap with starch to give a sol of high viscosity appears to be characteristic of only starch amylopectin. Heald suggests that the viscosity increase caused by the addition of 12 per cent. sodium oleate on the weight of the starch in a 0·5 per cent. sol might be used as a method of evaluation. This work and its later extensions mentioned above open up a further field of research on the use of starch in the paper industry.

A starch swollen with sodium silicate, can be entirely precipitated in the fibres, because when the web is dried by passing it over drying cylinders, the raw starch mechanically retained by the fibres is heated sufficiently to gelatinise it. The largest granules are readily retained, but many of the smaller ones are lost in the back water, and this loss may amount to between 10-30 per cent. of the total starch. On bursting, the contents of the granules pass into solution in the water retained in the web and spread over the fibres; on removing the water a strong continuous film over the surface is left. Some granules, however, escape gelatinisation and serve no useful purpose.

Treatment with sodium silicate swells the starch granules to many times their original volume, thus leading to greater mechanical retention, and, in addition, the glutinous nature of the

swollen granules serves to increase their retention; thus the mineral-starch process gives little or no loss of starch in the back water. The addition of starch paste to the beater leads to a large loss, as only the empty sacs are retained in the web, the soluble amylose being carried away in the back water.

The properties of rice, wheat, maize and potato starches have been examined by Wredé,⁹ who finds that wheat starch is absorbed by the fibres to the greatest extent but that maize is to be preferred on account of its greater gelatinising power and cheapness.

More work is required on the effect of starches on the retention of the fillers for there is a wide discrepancy of opinion on this effect. Some workers^{2, 16-19} consider the use of starch in the beater improves retention whilst other workers²⁰⁻²⁵ have not found starch beneficial in this respect. Indeed W. R. Willets²⁵ considers that an actual decrease in retention is brought about by the use of starch, certain starches having a more marked detrimental effect than others. He tentatively suggests that the starch, acting as a protective colloid, maintains the filler in such a well-dispersed state that it cannot be coagulated and fixed on the fibres, but passes through the filter mat of pulp initially formed on the wire.

The so-called thin-boiling starches may also be used in the beater. The diffusion of the soluble portion of a raw starch when gelatinised on the drying cylinders is a function of the water present and of the amount of starch which dissolves in it at the gelatinising point. By the use of soluble starch the granules are retained as with raw starch, but on passing over the drying cylinders practically all of it passes into solution and spreads over the fibres and through the interstices of the paper. Furthermore, as the moisture rises to the surface of the paper, the very soluble starch comes with it and gives an excellent surface finish. The nearer the starch solution approaches a true colloidal solution, the better is the effect and the greater is the surface area covered.

As the chief function of starch is to act as a fibre-to-fibre bonding agent at the point of contact of two adjacent fibres, it can only function in this manner where it contacts simultaneously two contiguous fibres. As a result, highly dispersed starch solutions are most effective in high-density sheets and least effective in low density sheets.¹² On the other hand poorly dispersed starch suspensions which are composed predominantly of swollen starch granules are most effective in low-density sheets and least effective in high density sheets.

Kerr has introduced a maize starch modified with chlorine

which is claimed to give an overall favourable efficiency compared with pregelled potato or cassava starch products, and to have such good redispersing properties that it can be added to the pulp after leaving the beaters but prior to entering the Jordan disintegrators. This allows easier control of the tensile strength as more or less size can be added at the Jordan disintegrators to remedy defects in this property but this would be less readily carried out by addition to the beater.

W. A. Scholten's Chem. Fabr.¹⁰ have covered the addition of a cold-swelling starch, in amounts up to 5 per cent., to the paper at any stage of its manufacture. If desired, it may be added in a dry state to the beater.

For this process the soluble starches produced by enzymes are preferable to the thin-boiling starches produced by acid treatment, as the latter are not so completely depolymerised as the former, and show retrogradation. For these reasons, thin-boiling starches made by acid-treatment do not give such a perfect film over the fibres as the enzyme-solubilised type, nor do they coat the fillers so effectively.

Retrogradation shown by starch is one of the factors militating against the successful use of precooked and redried starches for, when gelled, the amylose portion may precipitate on ageing and cooling and cannot be redispersed except by means of autoclaving or the action of an alkali. Thus precooked starches redispersed in water give a lumpy granular paste quite dissimilar to freshly prepared starch gels. This may lead to better retention, but gives poor dispersion throughout the web so that poor overall efficiency results.³¹ Overgrinding the dried product may reduce its retention in the web at the wire so that particle size of pregelled, redried products must be closely controlled.

The use of soluble starch also eliminates a fault sometimes encountered, viz. that caused by a local concentration of starch which, on the drying cylinders, gives a spot that is transparent when examined in transmitted light, the so-called 'slime spots,' 'windows,' or 'shiners'. This fact is referred to again below in connection with the fancy effects that are obtained by deliberately causing 'shiners' to appear in the paper.

With pregelled products borax is often introduced partly to act as a wetting-out agent and partly to facilitate redispersion of the insolubilised amylose by virtue of its alkaline reaction. Pregelled products are best made from potato or cassava starches, the final product containing a small amount of dispersing agent as they are more viscous, thus giving greater retention and retrogradation is less pronounced with these starches than, for example,

with maize starch. Such products have relatively high efficiency as beater sizes when properly used, but further mechanical dispersion may take place in the beater and they tend to give rise to trouble when trying to reconstitute the starch paste. The particles first in contact with water swell rapidly and the thick mucilage opposes the passage of water to the dry powder in the interior and 'balling' takes place. These lumps are broken down with difficulty. Similar trouble has been experienced, and overcome, in the preparation of dry adhesives (see p. 156).

Papers sized by the mineral-starch process, although quite 'soft' to the tongue, give excellent printing surfaces. The use of resin size in conjunction with the mineral-starch size is considered by some to be essential for writing papers, the latter size acting as a partial substitute for the more expensive resin size.

The mineral-starch sizing, used as an auxiliary agent to resin sizing, acts as a protective colloid to the resin, which is precipitated in a more finely-dispersed state, and to a more homogeneous distribution of the resin over a wider surface. Here again the use of soluble starches gives the best protective effect, as a true colloidal solution of the starch is obtained with high protective powers. Wredé⁹ considers that in sizing the starch should be thoroughly cooked with application of the warm paste to the fibres. The addition of a wetting agent increases the absorption of the starch and assists dyeing, but for papers requiring water resistance, e.g. posters, montan wax should be used.

The 'handle,' hardness, and capacity of the paper to take a high 'finish,' are all held to be improved by the addition of starch, and if for any reason the preparation of stock cannot be carried out to the desired extent, the quality of the sheet may be improved by adding starch. C. F. Cross and E. J. Bevan,⁵ however, consider that starch is at best only a substitute for thorough beating, and in many cases is less economical.

Calender Sizing.—In some cases the 'web' of the paper is formed and before the sheet is thoroughly dried it passes through a size solution in one of the calender boxes, the process being known as 'calender sizing'. All types and modifications of starch and starch products are very widely used in this process depending on the desired final result. As in textile sizing (see p. 263) the amount of starch in the finished product will be largely determined by the viscosity of the solution and hence by the 'pick-up' of the web and the use of thin boiling starches, having higher solids content for a given viscosity, leads to a much higher amount of starch being present in the final sheet. The process is largely used in paper board mills and is designed to improve the surface

of the sheet and prevent 'fuzz' or a hairy surface. A balance has to be struck in practice between the degree of modification and the amount of starch used as, in general, the greater the degree of modification the less the resistance of the starch film to abrasion or 'scuffing'. Therefore the starch is modified to the point where its viscosity allows an adequate amount of starch to be picked up but where it still retains a reasonably good scuff resistance.

When it is desired to produce a paper board suitable for printing, a highly modified starch is used at about 15-20 per cent. concentration so that the ink resistance and 'pick' is improved and the penetration of a portion of the starch solution to the interior of the sheet leads to some increase in bursting strength. Ingredients such as emulsified waxes are sometimes added to the size to obtain special effects and some makers sell starches with these ingredients already incorporated in the same way as the speciality laundry starches are marketed (see p. 287).

Tub Sizing.—For the preparation of papers intended for use in the production of ledger books, bonds, and other high-class paper, the process of tub sizing is carried out to give the required finish. This process consists essentially in running the paper through a bath of the size, and drying.

Such papers are never used for printing, but only for high-grade writing papers. Certain pigments are incorporated in the paper, which is then tub sized, china clay being used in England and chalk in America, where supplies of china clay have to be imported. It follows, therefore, that in America a neutral or slightly alkaline size must be employed. The function of the pigment is twofold: it assists the rapid absorption of writing ink, and it gives a surface with a better appearance.

The use of starch for tub sizing has been followed by R. M. Cobb and co-workers.⁶ The specific gravity of the various sizing agents must first be considered, and it will be found that more starch will have to be used than casein, the specific gravities of the two substances being approximately 1.62 and 1.26, respectively.

He and Lowe⁷⁻⁸ give a very simple formula connecting the depth of penetration in cm. (d), the paper-pore radius in cm. (r), the surface tension of the starch solution in dynes (σ), the contact angle taken up by the liquid in contact with the solid (θ), the time of penetration in seconds (t), and the coefficient of viscosity in poises (μ) where μ for water = 0.01006 poises at 20° C. This relationship takes the form $d^2 = \frac{r\sigma \cos \theta t}{2\mu}$. From inspection it will be seen that, other things being equal, the degree of penetra-

ion of starch into the sheet at the press varies inversely as the square root of the viscosity of the starch dispersion. The use of thin-boiling starches is therefore indicated.

Native starch, being too viscous for tub sizing in particular, is generally treated to reduce its viscosity and Kerr summarises the desirable properties of starch for the tub-sizing purposes.

1. High solubility for a relatively high-molecular magnitude.
2. Lack of separation of insoluble or retrograding phase.
3. Small increase in viscosity with decrease in temperature or increase in concentration.
4. Continuity of the film formed.
5. High protective colloid effect (especially desirable in surface-coatings).

From these it follows that, to obtain a more efficient size that either :—

1. The starch should before final modification to this usable viscosity, be pretreated or fractionated to remove the more linear fractions ;
2. Oxidised or properly dextrinised, or otherwise treated, to permanently solubilise the unstable amylose portion, or
3. If the paper maker enzyme-converts the starch to a suitable viscosity, then conditions should be established to preferentially degrade the amylose fraction into low molecular weight bodies with a minimum degradation of the amylopectin portion.

Coated Papers.—When the sheet is first formed and a size-filler mixture brushed, sprayed or applied by highly polished rollers to the sheet, dried and calendered, the product is known as 'coated paper,' which probably offers by far the biggest outlet for starch in the paper-making industry ; at least 50 per cent. of the coated paper made contains starch as the coating medium. Coated paper made by the process is known as '*brush coated paper*'. The latest process is that covered by the Massey patents, which constitute a triumph of chemical engineering rather than of chemistry.

The fillers, e.g. china clay, lithopone, blanc-fixe or chalk, are used in conjunction with starches, generally modified by the hypochlorite process. Other modifying agents may be used and certain acids have been successfully employed by the author. The coating mixture, which may also contain a coloured pigment, is brushed onto a travelling sheet, and the product, after drying and calendering, has a highly finished appearance. This class of paper finds application in photogravure work, fancy cartons, and true art papers which are relatively resistant to the penetration

of printing inks thus allowing better reproduction of photographic designs.

Shaw and co-workers¹¹ found that modified starches had not quite as strong adhesive quality as casein or glue, but all coating containing 18 pts. of starch to 100 pts. of clay were well bound to the body papers. Starch had the best clay-suspending properties, and when coated papers were printed by the half-tone process all three coating mediums were equally good although the starch-bound coatings appeared to absorb somewhat more ink.

G. E. Price,¹³ who has examined various types of starch products for paper coating, considers that they are substantially comparable with casein for this purpose, except as regards waterproofness. The modified starches were found to be superior to untreated starches for this purpose. J. P. Casey¹⁴ has also examined the uses of ordinary, chlorinated and enzyme-converted starches in beater, calender and tub sizing, coating and pasting operations. The effect of oxidised starches and very mild alkalis, such as borax, sodium silicate or phosphate, on the apparent viscosity of clay slips for coating was also examined by this worker. In his full discussion of all this work he makes recommendations as to the most suitable type of starch for the various conditions of application and for obtaining such characteristics as increased burst-, tensile- and fold-strength, sizing, printability and resistance to picking.

When clay or other filler is worked into a paste with water the amount of the latter present, for brush coating, should not exceed 55-60 per cent. as the drying time is then extended and less clay or filler is applied to the sheet. Equal parts of clay and water, however, form a thick, unworkable dough but protective and dispersing agents alter the characteristics to such an extent that such a mixture can be brushed on. One of the best agents to obtain this thinning effect is casein, which makes the coating quite fluid when present to the extent of only 5-10 per cent. Highly chlorinated starches used to the extent of some 15-22 per cent. on the weight of clay bring about a similar thinning and have very good adhesive properties. Such coatings are more resistant to bacterial and fungal attack but, as stated above, less waterproof. If the starch/clay ratio is increased loss of gloss occurs and a duller sheet is produced. Furthermore, the coating increases in viscosity increasing the difficulty of application. This cannot be overcome by reducing the viscosity of the starch solution by more drastic modification of the starch as this, in turn, leads to a loss of adhesive strength.

The amount of starch used by the paper industry has not been computed. Its use suffered from early workers not appreciating the above points, but it will undoubtedly expand in the future, chiefly because of the introduction of machine-coating. About 30,000,000 lb. of casein are used annually for paper coating, but starch probably will not reach this figure due to its greater water sensitivity, greater brittleness and lower grease resistance. The wet adhesive strength of starches is low being somewhat inferior to casein laid down from an alkaline solution without hardener and much inferior to aged, hardened caseins. There are, however, various hardening agents for starch, which will also improve its water resistance so that one of its chief drawbacks may soon be overcome.

It should be remembered when using starch solutions that mechanical action or excessive heating can cause disintegration of the structure of the paste leading to a loss of viscosity and adhesive strength. Acid-modified starches, of the same hot-paste viscosity as chlorinated starches, yield coatings more plastic in behaviour and with less adhesive strength than those from chlorinated starches, due to their greater tendency to retrograde after cooking and cooling. Kerr³¹ suggests that the explanation lies in the mechanism of modification in the two cases. With acid-modified starch the paste viscosity falls by virtue of a scission of glucoside bonds between the glucose units of the starch molecule weakening the physical structure. Further action leads to a decrease in average molecular size with concomitant loss of adhesiveness. Kerr considers that considerable degradation of amylopectin occurs before there is an appreciable breakdown of the amylose chains since he finds the amount of amylose precipitated by butanol increases in the intermediate stages of the hydrolysis to above that for untreated starch showing the amylopectin is degraded to a linear component. In the chlorination process, however, he finds the butanol precipitate decreases as the reaction proceeds but those properties dependent on the amylopectin portion of the starch are not affected. Kerr and Schink,³¹ in their unpublished work, find amylopectin separated from starch to be too viscous to give a clay coating when used at 15 per cent. on the weight of clay. As addition of water to lower the viscosity leads to poor adhesion they conclude that some modification of the amylopectin portion is desirable.

The amylose fraction could only be used at high temperatures (70° C.) and in low concentrations but proved to have higher binding strength than the amylopectin fraction at equivalent concentration. It appears preferable, therefore, to start with the

whole starch, rather than the separate components, and to modify this in such a manner that the greatest reduction in viscosity for the least reduction in molecular size is obtained.³³ a result which would be produced if the amylose could be preferentially degraded as pointed out by Kerr.³⁴

A considerable degree of preferential degradation of the two components can be brought about by the use of the appropriate enzymes. Thus β -amylase will completely degrade amylose to maltose but the amylopectin portion is degraded only to 'limit dextrins' (see Vol. I). Maltose, however, has no adhesive value and its production means virtually replacing a portion of the adhesive present in a coating with a non-adhesive, water-sensitive material. Although α -amylase will produce dextrins from amylose it also attacks and degrades amylopectin so that its action is somewhat similar to that of an acid and no advantage is gained by its use.

Kerr and co-workers³⁵ have attempted malt conversions at temperatures below the gelatinisation point of starch to avoid disorganisation of the molecule, but at temperatures high enough to favour the solution of the more readily soluble and apparently more simple amylose fraction. Corn starch was suspended in water to a concentration of 22° Bé and 1 per cent. of Pabst's Excise (a malt diastase preparation) added. The pH of the mixture was adjusted to 5, the temperature to 49° C. and the mixture stirred for 24 hours. The starch was then filtered off, resuspended and refiltered. The yield by this process is about 80 per cent. of modified starch. In spite of the fact that, as expected,³⁶ the residual starch shows a 5 per cent. lower 'conversion limit' with β -amylase than the parent starch by the method of Kerr and Schink³⁷ the modified starch liquefies at a faster rate in malt diastase conversions similar to those used in practice to produce thin-boiling starch pastes for the sizing of paper and textiles.

Starches converted by normal enzymic processes are distinctly more plastic in coating mixtures than such mixtures made with chlorinated starches. The use of special 'fluxing' agents with clay allows the use not only of the enzyme-converted starch products but also of other modified starches and starch products of high adhesive strength. Thus certain torrefaction dextrins can be used,³⁸ also starch treated with acetic acid or the 'peroxide' treated maize starch.

In the newer *machine coating process* the coating is applied to the web before it is completely dried, thus eliminating an operation and embodying the coating process in the production process. As water is already present in the web in this process it is desir-

able to add as little more as possible in the coating operation. Hence the total solids of the coating may be as high as 60 per cent. This demands an adhesive of low viscosity such that one part with two parts of water gives a fluid sol since much of the water in the coating will be required to preflux the clay. Casein finds favour on this account, but there appears to be a possibility that 'peroxidised' maize starch and special dextrans may be elaborated in the near future to offer competition to casein in this process.

C. C. Kesler and E. T. Hjemstad³⁸ have introduced a urea-formaldehyde-modified starch mixture for coating work.

They find that a starch which has been treated to render it suitable for coating work when heated with urea formaldehyde precondensate under acid conditions at a definite hydration temperature gels excessively in the early stage of the reaction. Continued heating, however, brings about a reduction in the viscosity to that of the original starch. The product now shows no tendency to gel, has increased cohesiveness and has less free water present. The product also has the valuable property of water resistance, the clay being bound firmly to the paper even when the coating is wet. Such water-resistant coatings should not be confused with water-repellent coatings, the latter not being wetted when brought into contact with water whereas the former will absorb water, but the wet coating still adheres firmly to the paper.

The water resistance can be varied by variation in the pH value, cooking temperature and time, drying temperature and resin content.

Such starch-resin films were found by these workers to exhibit a decreased shrinkage on drying. A thin layer of cooked starch paste will give noticeable shrinkage on drying, this shrinkage being apparently greater with starch than with many other organic film-forming materials. Dry starch films are very brittle and readily shatter when dried to low humidities. The internal strains set up on drying various materials and their influence on the adhesive strength of the material has been discussed on p. 132. A reduction in shrinkage and therefore in the development of internal strains by the resin reaction leads to a greater adhesiveness in the starch coatings prepared by the above method.

The water-resistance and shrinkage of films of starch for use in paper coating have been evaluated by these workers³⁸ by the use of two novel methods. To evaluate water resistance a 50 w. 110 v. electric light bulb is dipped into the coating mix and dried under specified conditions. The current is switched on for a definite period of time and the maximum temperature developed is below

125° C. The bulb is removed and attached to a variable speed motor by means of a Gooch crucible adaptor, and rotated against a circular brush immersed in 300 c.c. of clear, cold water for a definite time interval, e.g. 10 minutes. The turbidity of the water, measured nephelometrically, is inversely proportional to the water resistance. To assess the shrinkage on drying they measure manometrically the change in volume of an inflated gas-bag, which takes place after dipping it in the coating mixture and drying under appropriate conditions. They obtain the formula $S = 0.6845 - 0.67 \log v$, where v = change in volume of the bag due to the drying of the film, to express the shrinkage (S) of the film on drying.

Miscellaneous.—When choosing a starch for paper-making freedom from specks is desirable, and, as stated above, if it is to be added to the beater as raw starch, a thin-boiling variety is preferable. If, however, the starch is gelatinised before adding to the beater, one which gives a stiff paste is best. On the Continent potato starch is widely used; in England maize starch is favoured on the price basis; and in America unmodified maize and tapioca are widely employed. For high-grade papers many manufacturers prefer to use rice starch, which they add to the beater in the raw state. Owing to the small granule-size of this starch it can be uniformly distributed throughout the web, and on passing over the drying cylinders the granules burst and give a good tenacious paste. The price of this starch precludes its use for anything but the best grades of paper.

After the paper has been formed it may be required to bond together several plys of it to obtain thicker sheets. Bristol board and similar types of products, for example, visiting cards, show-cards, post-cards, or multiple wrappers for transport, are produced on this principle, and the adhesives chiefly used are based upon starch. The main points to be observed in using such adhesives are discussed in Chapter 8, Part II, and the consistency, as will be seen, may vary from thick viscous pastes to free-flowing liquids, the former being applied by rollers and the latter by brush. The amount of water in such adhesives, and the viscosity, must be strictly controlled or warping on drying will occur, and too great a penetration will leave no adhesive between the interfaces to act as the bonding agent.

Some of these adhesives contain a little alkali or borax, and trouble may be experienced if a change is made from one grade of paper to a lower grade, the adhesive being found to lose its effectiveness after a part of the 'run' has taken place. The main reason for this behaviour, when it occurs, is that the lower-grade

paper may have a more acid reaction, and the bleeding back of the acid substance into the slightly alkaline adhesive neutralises the acid and destroys the adhesiveness. The pH value of the adhesive has also to be carefully controlled when foils or coloured paper are used to cover cardboard, as corrosion and discoloration may occur in addition to the trouble mentioned above.

Starch is often added to paper to make it crackle, and novel effects can be obtained by varying the kind of starch, amount, and method of adding it. Fancy effects, e.g. paper appearing like parchment, and covered with blotches that appear transparent or less opaque than the main body of the paper, is obtained by putting an excess of unswollen starch into the beater, so that when bursting on the drying cans a large number of 'shiners' or transparent patches are produced by masses of the granules bursting in close proximity to one another.

Certain modified starches are met with in the paper trade, such as Paperine, Flourine, and Amijel, which impart special characteristics, such as increased 'burst' strength or apparent hydration, and permit of easy removal of water from the wet web of paper.

A. Frieden³⁹ has pointed out that the use of starch in paper making does not increase the bacterial content (see p. 303) even if no bactericide is used, and starch is probably superior in this respect to glue or casein.

To sum up, the paper industry consumes starch products as beater, calender, tub, and coating sizes, and as adhesives. Starch finds use in board mills to obtain a desired finish; in 'tag,' Bristol board and cover mills for obtaining increased strength, stiffness, finish, and formation of the multi-layer; in sulphite and rag-bond paper mills for improving the 'burst' strength; in Kraft paper mills for sizing, increased 'burst' strength, to impart rattle and a desirable finish; and finally, in book or printing papers for strength and 'fuzz' control. The control of 'fuzz' is important where a large quantity of paper has to be handled in a confined space, as the tiny fibres (or 'fuzz') fly off and affect the health of workers. It also has a large influence on the cleanliness of the printing as the speed of this is constantly increasing.

REFERENCES

1. H. WREDÉ, *Wochbl. Pap.*, 1913, **44**, 835.
2. TH. E. BLASWEILER, 'Use of Sodium Silicate for Sizing Papers,' Constable & Co., London, 1926; *Chem. Zentr.*, 1925, **2**, 1235.
3. A. LUTZ, *Ber. Hauptvers. Verein. Zellstoff. Papierchem.*, 1907; *Papier Zeit.*, 1908, **33**, 314, 1022, 1062, 1098, 1142.
4. ANON, *Paper Trade J.*, 1927, Dec. 1st, p. 51.

5. C. F. CROSS and E. J. BEVAN, 'A Text-book of Papermaking,' 5th Ed. E. & F. N. Spon, Ltd., London, 1920.
6. R. M. COBB, D. V. LOWE, E. POHL, and W. WEISS, *Paper Trade J.*, 1937, **105**, 33; *TAPPI*, 105.
7. R. M. COBB and D. V. LOWE, *Paper Trade J.*, 1934, **98**, No. 12, 43.
8. R. M. COBB, *ibid.*, 1935, **100**, No. 16, 42.
9. H. WREDÉ, *Papier-Fabr.*, 1928, **26**, 301.
10. SCHOLTEN'S Chem. Fabr., E.P. 380,674, 1931.
11. M. D. SHAW, G. W. BICKING, and M. J. O'LEARY, *U.S. Bur. Stds. J. Res.*, 1930, **5**, 1189.
12. J. P. CASEY, *Pap. Ind. and Pap. World*, 1945, **26**, 1277.
13. G. E. PRICE, *Paper Trade J.*, 1941, **113**, 17.
14. J. P. CASEY, *ibid.*, 1942, 114, *TAPPI Sect.*, **77**, 107.
15. R. W. KERR, *Paper Trade J.*, 1942, **115**, 30, 292. (Latest concepts of starch chemistry applied to tub-sizing.)
16. F. W. BAILEY, *World's Paper Trade Review*, 1928, **85**, 260, 262, 264.
17. — *Paper Maker*, 1928, **75**, 145.
18. — *Pulp Paper Mag. of Can.*, 1928, **26**, 871.
19. K. ATSUKI and M. NAKAMURA, *Cellulose Ind.* (Tokyo), 1927, **2**, 46; via C.A. **22**, 163.
20. Anon., *Woch Papierfabr.*, 1915, **46**, 2387; 1916, **47**, 544.
21. H. ROSCHIER, *Papierfabr.*, 1926, **24**, *Tech.-Wiss Teil*: 348, 363, 384.
22. — *Papeterie*, 1927, **49**, 201.
23. — *Paper Trade J.*, 1927, **85**, No. 22, 51.
24. Anon., *Paper*, 1917, **18**, No. 6, 11.
25. W. R. WILLETS, *Paper Trade J.*, 1935, Sept. *TAPPI Sect.*, 177.
26. H. N. LEE, *ibid.*, 1938, **21**, *TAPPI Sect.*, 319.
27. B. W. ROWLAND and J. V. BAUER, U.S.P. 2,113,034; 1938.
28. B. W. ROWLAND, U.S.P. 2,207,555; 1938.
29. A. M. HEALD, *Paper Trade J.*, 1941, **113**, 39.
30. C. C. KESLER and W. C. BLACK, *Paper Trade J.* 1942, **114**, *TAPPI Sect.*, 247.
31. R. W. KERR, 'Chemistry and Industry of Starch,' Academic Press, N.Y., 1944.
32. R. W. KERR, U.S.P. 2,108,862; 1938.
33. R. A. DIEHM, *Tech. Assoc. Papers (TAPPI)*, 1937, **20**, 279.
34. R. W. KERR, *Paper Trade J. (TAPPI)*, 1942, **115**, 30.
35. R. W. KERR, H. MEISEL and N. F. SCHINK, *Ind. Eng. Chem.*, 1942, **34**, 1232.
36. — O. R. TRUBELL and G. M. SEVERSON, *Cereal Chem.*, 1942-3.
37. — and N. F. SCHINK, *Ind. Eng. Chem.*, 1941, **33**, 1418.
38. C. C. KESLER and E. T. HJEMSTAD, *Paper Trade J. (TAPPI)*, 1945, **120**, 160.
39. A. FREDEN, *Paper Trade J.*, 1940, **110**, 29.

ADDITIONAL REFERENCES

- H. WREDÉ, *Papier-Fabr.*, 1922, **20**, 1429. (Discusses use of starch in paper-making.)
- H. WAGNER, *Chem.-Ztg.*, 1923, **47**, 249. (Discusses adhesives for the paper industry.)
- E. TROMP, *Papier-Fabr. Ver. Zellstoff-chem.*, 1925, **23**, 109. (Discusses use of starches in the paper industry.)
- J. TRAQUAIR, *Paper*, 1918, **21**, 68, 70. (The function of starch in beater-sizing discussed.)
- W. A. NIVLING, *Paper Trade J.*, 1922, **75**, 32. (Discusses the use of starch in paper sizes.)
- J. J. SAXL, *Paper Trade J.*, 1937, **105**, No. 13, 46. (Instruments for testing starch for use in paper-making are discussed.)
- C. G. WEBER, M. D. SHAW, and M. J. O'LEARY, *U.S. Bur. Stds. Misc. Publ.*, 1935, **M150**, 7. (Sweet potato starch is suitable for beater-sizing of paper.)

- J. STRASSER, *Paper Trade J.*, 1936, **102**, No. 17, 29. (General.)
- P. MURANYI, *Chem. Zentr.*, 1939, **110**, 1, 3477. (Starch treated with arylsulphonchloroamides used to size paper in conjunction with glue.)
- H. NOUVEAU, *Papier*, 1939, **42**, 383, 465. (Uses of potato starch and derivatives in paper-making.)
- J. ROBERTS, *Proc. Tech. Sect. Paper Makers' Assoc.*, 1939, **19**, part 2, 439. (Uses of various starches in paper-making discussed.)
- F. HOLT, *Paper Ind. Paper World*, 1939, **21**, 332. (General.)
- STEIN HALL MFG. CO., U.S.P. 2,197,754. (Laminated paper and paper-cloth made by applying ungelatinised starch in a starch gel to surface and then gelatinising *in situ*.)
- H. N. LEE, *Paper Ind.*, 1937, **19**, 785. (Photomicrographs in colour for investigating use of starch in paper-making.)
- A. H. KELLING (to Corn Prod. Ref. Co.), U.S.P. 2,171,796, 5/9/1939. (Preparation of modified starch for paper-sizing.)
- C. A. BRIGGS and J. L. MCCARTHY, *Pap. Trade J.*, 1942, **114**, TAPPI, 37, Jan. 22nd. (Evaluation of starches for paper trade by viscosity measurement.)
- AMERICAN MAIZE PRODUCTS CO., U.S.P. 2,319,637. (Acid modified waxy maize starch used for paper-sizing.)
- H. T. RUFF, U.S.P. 2,140,394, 13/12 38. (Aqueous slurry of starch and mineral filler heated together to coat particles and used for paper loading.)
- H. SCHOPMEYER and G. E. FELTON, U.S.P. 2,354,838, 1944. (Waxy starch oxidised with sodium hypochlorite at pH 7-11 and 100° F., filtered and washed. Used as adhesive or coating ingredient.)
- E. R. EDSON and C. Q. IVES, U.S.P. 2,337,458, 1943. (Engine sizes by adding dry powder mixture of rosin and acidic starch conversion product in a bag which is disintegrated.)
- U.S.P. 2,337,459. (Engine sizes by adding a bag of the acidic, calcined starch described in U.S.P. 2,239,814 and beating to homogeneity.)
- R. W. KERR and N. F. SCHINK, *Paper Trade J.*, 1945, **120**, 86, 88, 90, 145. (Discusses amylose and amylopectin in relation to paper sizing. Pyrodextrins give mixtures with clays having relatively low viscosity, low plasticity and high adhesive value and are superior to starches.)
- R. W. KERR and N. F. SCHINK, *Paper Trade J.*, 1945, **120**, 86, 88, 90, and 145. (Discusses amylose and amylopectin in relation to paper sizing. Pyrodextrins give mixtures with clays having relatively low viscosity, low plasticity and high adhesive value and are superior to starches.)
- H. B. T. STANLEY, *Austr. Pulp paper Ind. Tech. Ass. Proc.*, 1948, 2, 187. (Surface sizing with starch.)
- J. W. EVANS, U.S.P. 2,400,402, 14/5/1946. (Acid modified starch with triethanolamine stearate for paper coating.)
- W. J. CRAIG, *Paper Trade J.*, 1949, 128, *Ind. Dev. Sect.*, 246. (Paper coating with coloured, enzyme-converted starch.)
- J. C. MARRONE, U.S.P. 2,433,285, 23/12/1947. (Mixture of cold swelling and raw starches used for tub sizing.)
- TAPPI Monograph No. 3, 1947. (Whole field of starch in paper discussed by many authors. A number of chapters have lists of references and a list of coating patents is given.)
- C. C. KESLER, J. E. KILLINGER and E. T. HJERMSTAD, *Paper Trade J.*, 1946, **122**, No. 3, 39. (Moisture sorption and shrinkage of starch films on drying. Amylose containing starches show high, and amylose-free-starches low shrinkage. Effect of resins discussed.)
- O. R. STEFFENS, *Paper Mill News*, 1950, **73**, No. 1, 16, 18, 22. (Starch as a beater additive and its effectiveness in improving sheet properties reviewed.)
- R. W. KERR, *Paper Trade J.*, 1950, **33**, TAPPI Sect., 268. (Starch dextrinised with AlCl_3 used for machine coating.)

CHAPTER 12

THE TEXTILE INDUSTRY

Sizing of Yarns.—The practice of sizing cotton, linen, or viscose rayon in the form of hank or warp has the primary object of causing the fibre to absorb an adhesive like starch or an allied product. This treatment imparts to the fibre a much greater tensile strength, and also resistance to the abrasive action of the parts of the various forms of machinery that are employed in making the yarn into a woven fabric.

The practice of efficient sizing can still be regarded as an art, and it is one which only in recent years has been approached in the true spirit of scientific inquiry. What was once the most empirical of operations, only carried out successfully by an operator of many years' practical experience, is gradually being based on some measure of scientific control. In spite of this technical progress, most sizing operations are controlled by practical experience rather than by scientific theory. Whilst the physical and chemical properties of starches and allied products are well known, the condition of application and the choice of the correct composition of a sizing 'mix,' are matters for practical experience.

This section deals solely with a brief résumé of the general principles underlying the practical usage of starch products in sizing, and standard works should be consulted if further practical details are required.

Reference to the section on 'finishing' will show that it is closely related to sizing, as similar materials are used for each operation. The main differences between the two processes are, firstly, sizing is only practised on warps and to some extent on yarn, and 'finishing,' for practical purposes, is the application to fabrics. An important difference between sizing and 'finishing' is that, generally speaking, the size must be removed before the woven fabric is in a fit condition to be dyed or properly 'finished,' whilst the 'finish' can with considerable advantage be regarded as permanent. In the case of fabrics that are to be dyed direct, the sizing material must be properly removed (see Desizing, p. 267), otherwise dyeing faults may occur owing to residual sizing

materials acting as a partial 'resist'. For example, the evils attendant upon using paraffin wax as a component of a size for cotton warps, when the woven fabric is subsequently to be dyed, are well known to many dyers.

Sizing.—There appear to be two schools of thought concerning the requirements of a sizing agent, one school maintaining that the size is best retained on the surface for obtaining the maximum effect, and the other that the size should penetrate the fibre and become a mechanical part of it. Those holding the latter view point out that starch retained on the surface is apt to be mechanically removed, or 'dust off,' in the weaving. Alternately, as high extensibility of the yarn minimises breakages, complete penetration gives the maximum extensibility with the same amount of size, bearing in mind that the size film is not so extensible as the fibre. A very dusty or 'flakey' size is, of course, very undesirable, and a size which combines a certain degree of penetration with adequate surface protection can be regarded as the most satisfactory from a practical point of view. In any case, the type of sizing employed depends upon the mechanical requirements of the yarn. Many agents other than starch products are in use for sizing various types of fibres, but starch paste, either alone or in a converted or solubilised form, is chiefly used on cotton and linen, and we shall confine our attention to these two.

Potato starch yields a more viscous paste, weight for weight, than maize starch, and this in turn gives a thicker paste than sago, which suffers from the defect that it breaks down on continued boiling to a much greater extent than the other two. The thicker the paste, the more of it is picked up by the fibres, as explained below, and allowance must be made for this fact when sizing with, for example, a sago paste, to get the same effect as with a potato-starch paste.

Generally, the strength of films obtained from starch size made by cooking the starch with water and then adding the softening agents is greater than the strength obtained by the use of modified thin-boiling starches that have received excessive treatment in manufacture, providing the same weight of starch is applied in each case (see below). It is safer, therefore, when a supplier of a satisfactory thin-boiling starch has been found, to obtain supplies from him rather than attempt to modify the starch in the works to match the quality used. A converted or modified starch is used to obtain penetration, because the viscosity of solutions of these preparations is much less than that given by untreated starch (see below). The degree of modification is sometimes expressed as the number of ml. of a starch solution of standard concentration

that will flow from a pipette in a given time, e.g. 90 degrees thin-boiling starch, etc. Such starches may be produced by oxidising agents (p. 153), acids (p. 147), or by enzyme action.

In sizing warps, the fibres lying side by side pass over beams to enter the hot size, and on leaving the 'sow-box' pass through rollers and over heated 'cans' or hollow rollers to be dried. The threads which are stuck together are then separated. In another process the 'ends' or lengths of yarn are sized and dried simultaneously, but separately.

Considerations influencing Sizing.⁹—For sizing, the starch is used in all stages of solution or dispersion, from thin watery solutions to highly viscous 'solutions'. The viscosity of a starch solution is a good index of its practical value for many purposes, but care has to be taken, for example, in the case of potato starch where a higher initial viscosity is generally combined with a tendency to 'boil thin' and thus alter the amount of starch, as such, which is applied to the fibres because the amount of size picked up by a yarn depends on the viscosity and not on the concentration. A glance at Table XII shows that the breaking load of films made from pastes of different starches at the same concentration depends on the film thickness which in turn appears to depend to a large extent on the viscosity of the paste.

As can be seen from the gelatinisation diagrams in Vol. I, the various starches do not gelatinise at the same rate, thus, for the same amount of boiling (providing the time of boiling is such to give less than the maximum gelatinisation possible with that particular concentration and starch), the extent of the gelatinisation and the viscosity, and hence the amount of size picked up by the cloth, may be different. Sago and tapioca gelatinise almost completely if the size is boiled for about two hours, and potato-starch size takes about the same length of time, although it is somewhat slower gelatinising in the early stages of the boiling, while maize is both slower and more difficult to gelatinise than the above starches, and the latter is also true of wheat flour. With maize and wheat, then, even thorough boiling does not give complete gelatinisation, so that the use of these two are probably confined to open cloths made from coarser yarns where a greater amount of size can be applied and, owing to the incomplete gelatinisation, is necessary in order to obtain good weaving.

Both potato and tapioca starches give more viscous pastes than sago starch even after prolonged boiling, and to obtain similar amounts of starch on the yarn in each case some 10 per cent. more sago starch should be used than in the case of the first

two starches. This increase in concentration increases the viscosity of the paste to a figure nearer to that of the other starches, so that nearly the same amount of size with a higher solid-content is picked up, giving a similar percentage of actual starch on the air-dried yarn. In stability of the boiled size, tapioca is probably better and less variable than sago starch, whilst potato starch is more variable and liable to change than either.

In sizing, the warp enters the size box and picks up an amount of size depending on the viscosity of the paste, it then meets the squeezing roller where some of it is squeezed off; but the more viscous the size, the less is the loss in weight and the heavier the 'finish'. Other factors, such as softness of the pressure bowls, running speed of the machine, and the pressure between the bowls, influence the 'finish'. It should be noted that although up to a certain point increase in viscosity of maize and potato starches leads to an increase in the amount of size retained by the warp, after this maximum is reached there is an irregular falling off.

Another factor of importance in sizing is the rate at which cotton yarn is wetted by the size. The average sizing preparations only wet raw cotton imperfectly, and to produce spontaneous wetting of the yarn by the addition of wetting agents an excessive amount would be required. F. D. Farrow and S. M. Neale¹⁴ have found that effective wetting of the yarn is promoted by using squeeze rollers and working 'at the boil'. The use of the higher temperature range is effective, not because of any marked alteration it induces in the surface tension of the size, but because it lowers the viscosity of the size and assists the escape of air bubbles.

Heavy pressure, slow running of the machine, or a double run through the sizing machine, lead to an increase in the area of warp threads covered by the size, all these factors favouring penetration. Drying on the hot cylinders or 'cans' also causes greater penetration than that obtained when the warp is collected wet, as the rapid cooling of the size in the latter case greatly increases the viscosity, which militates against penetration, the opposite effect being obtained in a short time on the drying 'cans'.

The effectiveness of a size depends upon its distribution and the adhesive character of the film, both factors which can be regulated to suit different conditions. By the use of hydrolysed starches the amount of solid matter in the solution can be increased without appreciably altering the viscosity or the penetrating power of the solution, leading to increased weight in the fibre and greater stiffness and bonding power of the solution.

M. S. Furry^{15,18} has examined many of the mechanical sizing and finishing properties of a number of starches and her results are summarised below :—

TABLE XII

MECHANICAL PROPERTIES OF STARCH FILMS AND SIZED CLOTHS
ARRANGED IN ORDER OF DECREASING MAGNITUDE

<i>Film Thickness from same Concentration of Paste.</i>	<i>Extensibility of Film and Sized Cloth.</i>	<i>Folding Endurance.</i>	<i>Stiffness, Pliability and Stretch of Cloth.</i>	<i>Breaking Load at same Concentration of Paste.</i>
Potato Canna Sweet potato Rice Corn Dasheen Wheat	Potato Canna Sweet potato Rice Wheat Dasheen Corn <i>N.B.</i> —Glycerine and turkey-red oil increase extensibility, Borax decreases it.	Canna Potato Sweet potato Corn Rice Wheat Dasheen <i>N.B.</i> —Values decrease with increasing film thickness and with addition of auxiliaries.	Sweet potato Rice (a) Wheat Dasheen (b) Corn Canna (c) Potato <i>N.B.</i> —(a) Thicker film; stronger cloth obtained; (b) Better penetration and greater stiffness than with canna starch. (c) Stiffer cloth.	Potato Canna Sweet potato Rice Corn Dasheen Wheat <i>N.B.</i> —All give approx. same breaking load if conc. of paste adjusted to give same film thickness. Breaking load increases with thickness.

Treatment of the starch with oxidising agents, acids or enzymes causes the films to be weaker, but as many of these products are of the 'thin-boiling' type a greater weight of starch per unit volume of size can be obtained. Thus, if the viscosity of a size made from a treated starch is similar to that of a size from an untreated starch the former will contain more starch, depending upon the extent to which it has been modified, and thus a thicker, and therefore stronger, film is obtained. As a greater amount of modified starch can be applied this more than offsets the loss in strength due to modification of the starch. If the starch is so modified that the viscosity of the size is low, and yet the concentration of starch in the paste is such that it offsets the loss in strength due to modification, then it penetrates better than untreated starch. The effect of humidity on the strength of starch films has already been discussed in Vol. I. Those starches showing lower folding endurance generally give stiffer cloths when used for finishing.

The Effect of Auxiliary Agents on the Properties of Sizes and Finishes.—A number of agents are added to sizes and finishes to obtain certain effects, more particularly from the point of view of 'handle,' or 'feel.' Small amounts of borax increase

the strength of starch films but larger amounts weaken it. The increase in film strength is also obtained, but to a lesser degree, by the addition of glycerine, but, in this case, increasing the amount of glycerine has a much lesser effect on the film strength than increasing amounts of borax whilst large amounts of glycerine have little more effect than small amounts.

Substances which are used to soften the films, such as tallow, castor oil, and glycerol, etc., cause a decrease in film strength if present in amounts over 4-5 per cent., a similar effect being shown at this concentration when waxes or soaps are incorporated. In the case of the last two auxiliaries the transparency of the film is also adversely affected. In small amounts soap and turkey-red oil appear to increase the strength.

Desizing.—For the sizing of warps on the slasher we have seen that various substances are used, e.g. starches, casein, gelatine, soaps and softeners, fillers such as clay, and certain inorganic salts. The presence of these substances may interfere with the subsequent treatments, such as bleaching, dyeing or printing, and in order that these processes may be more effectively carried out they are removed by the process known as 'desizing'. Efficient desizing should remove the whole of the size easily and without affecting the fabric in any way, and the place of desizing in the order of operations naturally depends upon the type of goods being produced by any one plant.

For removing starch sizes, the fabric is treated with agents to break down the starch molecule to a simpler type of molecule, e.g. that of dextrans or sugars, as these substances are more readily removed by washing than unchanged starch. For this purpose an inorganic acid, or an acid salt, may be employed. Boiling with water alone for a long time will bring about these changes, but the hydrolytic action is catalysed, or speeded up, to a marked degree by the presence of hydrogen ions. Although acids and acid salts can be used, saccharifying and liquefying enzymes are preferred by many workers, because they exert no deleterious action on the cloth. Other starch-solubilising compounds, e.g. certain swelling agents and oxidising agents, are also in use.

The use of diastatic enzymes in desizing fabrics is usually confined to textiles of the better grade, or to goods which are subsequently to be mercerised and dyed and, therefore, have to be quite free from extraneous matter if the fullest lustre is to be obtained. The best results in bleaching and dyeing depend upon efficient desizing of the cloth, as residual sizing agents make it impossible to obtain a well-penetrated and evenly-dyed material.

It may sometimes happen that owing to incorrect dressing, the 'handle' or feel of a finished fabric is not what is desired, and in such cases partial desizing or desizing followed by re-finishing may rectify the fault.

Hall has shown from Tschilikim's work that the complete elimination of starch from a sized fabric is difficult to accomplish by the older methods. Boiling a sized fabric in water followed by 14 hours' immersion at 30° C. did not remove the starch, nor did a 13 hours' treatment in a cold solution of a powerful wetting agent, nor 14 hours' treatment at 20° C. in a 0.4 per cent. solution of caustic soda. Treatment of the fabric, either with sulphuric acid, hot or cold, and strong enough to attack the fibre, still left some starch in the fabric. Complete removal of the starch, however, was claimed by the use of enzymes.

Considerable difficulty is experienced in removing unmodified starch sizes from rayon staple fibre cloths so that an undesirably long processing may be necessary before obtaining good elimination of the starch. The sized warps contain a variable amount of starch that is removed only very slowly by desizing with malt diastase and is affected only slightly by subsequent dyeing and scouring operations. The closeness of the structure of the cloth may, in many cases, impede the removal of the starch so that some workers favour the use of soluble starch or gum tragacanth.

Enzymes.—Enzymes have been defined as catalysts produced by living organisms. Many chemical reactions can be brought about under ordinary conditions of temperature by their use where otherwise high temperatures and powerful reagents would be required. They obey the laws of catalytic phenomena and are heat sensitive. Amylolytic enzymes, which are fully discussed in Vol. I, destroy starch, giving soluble substances of lower molecular weight, and in desizing they perform the same functions as acids in eliminating starch from a sized fabric, but are more rapid in their action, and are readily controlled; they have the additional advantages of specificity and of having no deleterious action on the fabric if used in excess.

Concentration, temperature, and hydrogen-ion concentration all play important roles in influencing the activity of any given enzyme, each one having its own set of optimum conditions (see Chap. 19, Vol. I. On a commercial scale an important factor is the speed at which an enzymic preparation acts. It is insufficient to be told that a certain preparation will convert many thousand times its weight of starch; the time taken to bring about the conversion must also be stated. Enzymes increase the reaction velocity of an action already proceeding, and the

amount of change brought about depends, up to certain limits, on the length of time the process is allowed to run. The rate at which such changes proceed depends on the concentration of the catalyst present.

As with ordinary chemical reactions, in the absence of a catalyst a rise in temperature speeds up the velocity of the reaction and up to a certain point this also applies to enzymes. Some of these substances have their optimum temperature in the region of 37°C ., but some can withstand temperatures up to about 93°C . The majority are destroyed with extreme rapidity after the temperature has exceeded the optimum, but a few take some time before they are thoroughly inactivated. Once they have been destroyed by heat they cannot be reactivated, and the deactivation by heat is much slower when dry powder preparations containing the enzyme are used. According to Gale, malt amylase loses 85 per cent. of its starch-degrading value in one hour at 60°C . and 72 per cent. in 30 minutes at the same temperature.

The $p\text{H}$ value of the medium is another important factor influencing enzyme action and in some cases the optimum value varies according to the source from which the enzyme is obtained. Apparently the more these substances are purified the more rapid becomes their decomposition, and it may be that the impurities present have some stabilising or protective action on the enzyme. J. E. Evans,¹³ for example, points out that the amylase preparation known as 'Rapidase' contains no albumins coagulable by heat, but these are present in other amylase preparations. This fact may account for the heat-resistance of Rapidase, and is indicative of the importance of the influence which may be exerted by extraneous substances on the reactions and activity of the enzymes.

Thus in one patent of Kalle & Co.,¹² enzyme preparations are activated by the addition of salts of phosphoric acid (except orthophosphoric acid), as little as 0.01 to 0.001 per cent. of pyrophosphoric acid being required. The action does not appear to be a buffering one, as it also occurs at the $p\text{H}$ value which is optimum for the particular amylase. The use of amino-diacetic acids and their salts is also claimed¹⁷ to give practically complete protection to desizing amylase preparations against the inhibiting effect of salts of heavy metals such as zinc and copper. A survey of the preparation and properties of amylolytic enzymes is given in Vol. I.

The Use of Enzymes in Desizing.—The usual method of desizing is to run the fabric to be treated over the singeing rolls, then past a steam box to stop 'sparking' or into a box contain-

ing the desizing enzyme solution. Alternatively, it may be passed into a bath of hot water which serves the double purpose of removing soluble inorganic salts and raising the temperature of the cloth to that of the desizing bath containing the enzyme, so that the temperature of the latter is not lowered by the passage of the cloth through it. After leaving the hot-water bath, the cloth immediately enters the desizing bath, and the process may be a continuous one or may be carried out on a jig. After treatment the cloth may be passed immediately to the washing machine or it may be piled and left overnight.

Generally 1 hour is allowed for desizing, but frequently the time may be extended to 10 or 12 hours. If the cloth is thoroughly 'wetted out,' so as to allow easy access of the diastatic solution to every part of the fibres, there is no reason why the desizing should not be completed in 15 minutes, provided the concentration of the diastase is somewhat increased. When a short time of treatment is desired it is preferable to work at a higher temperature. It should be noted that if the goods are allowed to lie in the piles overnight saturated with the diastatic solution, the actual temperature of the desizing is that of the room for the major portion of the time, as the temperature of the piles soon falls to that of its surroundings.

In the market preparations usually met with the amount of diastatic enzyme employed may vary between wide limits depending on the type of cloth, amount of size, and the activity of the preparation. About 5-8 lb. to 100 gall. of water may be used in some cases with a good malt, but a somewhat larger quantity may be required if the water is very hard, or the time is to be shortened by the use of a higher concentration at a higher temperature. When employing special preparations such as Rapidase, Polyzime-N or Diastafor, amounts in the region of 1-3 lb. per 100 gall. may be used. While standing overnight, the starch becomes thoroughly liquefied and readily washes out when the fabric is passed through the wash. After the desizing, the fabric may be prepared for dyeing or may be bleached. To ensure thorough penetration of the desizing liquor into a fabric of the tightly woven type, a wetting agent may be added to the bath; a heavy set on the pad-roller is desirable, the fabric being flexed as little as possible during desizing.

It sometimes happens that a fabric is given too harsh or too stiff a 'finish' to be suitable for sale, and then it may be stripped by a 1-2 hours' treatment with a warm diastase or protease solution, depending on the type of 'finish'. An alternative way of treating such a fabric is to pad it through a dilute solution of the enzyme,

and either plait it into a box, or batch it up warm and allow to stand for a few hours. At the end of this time it is dried, either on a frame, or by passing it over drying drums or 'cans,' when the 'finish' is found to be much softer owing to the action of the enzyme on the stiffening agent. This method is considered valuable for blotch prints, which often 'finish up' too stiff, and it saves two operations.

The Finishing of Textile Fabrics.—Most fabrics before they are finished generally lack the properties that make them commercially desirable as assessed by appearance, 'feel' or 'handle,' draping properties, and other physical characteristics. All textile fabrics, before they can be marketed, must receive some degree of 'finish,' which may range from a treatment with very weak solutions of starch or allied product through innumerable graduations to the 'back-filling' finishing method, for which a heavy, viscous 'starch mix' is used; this mix is pressed into the fabric, thus filling the spaces between the fibres which are themselves heavily coated at the same time. For the lighter type of 'finishing' the requirements may be quite the reverse, all the spaces between the woven threads being open, and individual threads being coated with a transparent flexible film through which any colour on the fabric can be seen to full advantage; for this purpose, the thin-boiling modified starches may be used.

The materials used in these processes, known as 'dressings,' are employed for stiffening, glazing, loading or weighting the fabric, and may be classified according to their origin or to the type of fabric to which they are applied, or, again, to the effect they produce.

The finishing of materials is an art in itself, and many manufacturers put the work of 'finishing' their textile materials into the hands of specialist firms. Much depends upon the mechanical aspect of 'finishing,' for the same dressing applied in different ways may give very different effects.

With dyed cloth the 'finish' plays an important role, but with a printed material the pattern is the most important part, although naturally the 'finish' must show this to the best advantage, and it is often said that a finisher is paid for his finger-tips, years of experience being required for a man to master the art.

If often happens that one dressing may be used for several fabrics, and then it becomes possible to classify these dressings according to the type of work for which they are used, for example, stiffening, glazing or imparting a soft 'handle'. For stiffening and glazing most of the common starches, dextrans, vegetable gums and gelatine may be used.

Shading ingredients (see p. 276) and antiseptics (see Chap. 15) are commonly incorporated in dressings, the former to improve the colour and the latter to prevent the growth of mould or mildew.

Adhesive Dressings.—Adhesive dressings are used when inorganic pigments are used as fillers, and their function is to retain the pigment and prevent ‘dusting off’. Vegetable glue, sold to the trade under a variety of trade names, such as Japan Glue, Arabil, Tragacanthine, Gummi Germanicum, was at one time widely used, and appears as whitish, translucent solid products, or in the liquid or paste form. It formed a substitute for gums, sizes and starch pastes in a variety of finishing processes. This class of compound is generally a treated starch, or a treated flour.

When making sizes enamel pans and rubber-coated stirrers are preferable, so that contamination with iron is avoided, for iron is detrimental to the colour of the product. The use of live steam is considered by some workers to give smoother pastes, but if this method is used the amount of water formed by condensation must be taken into account. If magnesium chloride is used as the swelling agent, then wooden vats heated by live steam may be used.

A vegetable gum, marketed under the name of Arabol, has been stated to contain approximately 55 per cent. dextrin, 25 per cent. maltose and 4 per cent. starch, the balance being moisture, and would appear to be an enzyme-treated starch.

‘Apparatine’ was first introduced by Gérard, who treated starch with caustic alkalis or carbonates.

The vegetable glue, made by the action of alkali on starch, is invariably neutralised, and instead of the mineral or organic acids generally used, a fat or vegetable oil which is readily saponified in the cold is sometimes used.

Dressings containing magnesium chloride have the useful property of absorbing moisture, so that even in the presence of a large amount of starch the fabric still has a fairly soft ‘handle’; but care must be exercised, especially with goods for export trade, because storage in a place of high humidity will lead to a greater increase of weight than is desirable.

Characteristics of Individual Starches. As starch is a very important ingredient of dressings for white goods, the properties of its different varieties are utilised with respect to the class of goods being dressed and the effect desired. The dressing may vary in consistency from a thin milky liquid to a thick, almost dough-like mass.

Farina or Potato Starch.—Of all the starches used extensively

in the textile industry farina or potato is the most viscous and most variable in properties. On storage the viscosity often decreases and this does not appear to be connected in any way with the presence of soluble impurities, for when these are removed the same phenomenon is shown. Farina pastes are considered in the trade to 'boil thin,' i.e. the viscosity falls off rapidly after reaching a maximum. This, as previously explained, is due in a large measure to breakdown of the structure of the paste on prolonged boiling and stirring, but after the farina pastes have been thoroughly boiled so as to obtain complete gelatinisation, the viscosities are higher than those of, for example, sago pastes of the same concentration, but variations in viscosity are greatly reduced.

Farina can therefore be used quite satisfactorily for sizing if tests are first made of the viscosity and the stability of the batch to be used, and the concentration and length of boiling of the paste controlled to give the best results. One method of overcoming the 'boiling thin' of starch paste is to make several successive batches of size which are immediately used after a short boiling. This, however, does not get to the root of the matter in that the product still has a variable viscosity and in use it is a competition between the sizer and the starch as to whether the former finishes the job before the viscosity of the latter changes. By adequate boiling and concentration adjustment the viscosity-variation is eliminated to a great extent. The passage of a potato-starch size or finish through a homogenising mill would probably overcome the 'thin-boiling' trouble and give a stable product.

To reduce the viscosity of farina pastes without lowering the solid-content, F. Ohl⁸ recommends the addition of a boiling 2-5 per cent. solution of dextrin, instead of water, when making the paste.

Potato starch or flour acts as a filler that is also flexible, and imparts a soft 'handle' to the goods being used, where opaque effects are desired. In conjunction with borax it gives a 'finish' of increased brilliancy. In this respect Japanese starch is considered by some workers to be inferior to American starch, and from 1933 for a few years the Russians offered a very good product superior to many starches on the market, although it ceased to come into the country about 1938.

Rice starch penetrates, gives a glazed and transparent finish, and weights the material well. It is of chief interest to the laundry trade, where it is used for stiffening, as it does not become limp in a humid atmosphere as do other starches.

Maize or corn starch gives a hard board-like 'finish' and is used extensively, either alone or in conjunction with potato starch, for stiffening piece goods.

Tapioca starch is softer than maize starch and gives a more transparent jelly; 'finishes' from this starch are more flexible and tough than those made from maize starch, whilst dextrins made from it are the strongest of all dextrins.

No amount of boiling will reduce the harsh 'feel' characteristic of maize and rice starches, but maize starch, partly converted to the soluble form by the action of hydrochloric acid, can be made to give a very similar effect to that obtained with wheat starch; the untreated starch, however, gives a thicker paste than wheat starch.

Sago starch has long been used in *cotton warp sizing*, and has been found satisfactory for several purposes, but in 'finishing' it is not widely used because, although it gives a thin, firm 'feel,' it tends to crack when folded. Bleached sago is reported to have been made in Lancashire 80 years ago.

When swelling or other agents are heated with starch suspensions degradation of the starch often ensued and, indeed, within limits, is often desirable in order to obtain the desired effect. If wheat starch is used, the 'mixes' will be found to require longer heating than those made with potato starch. In general, not less than $1\frac{1}{2}$ hours', and not more than $3\frac{1}{2}$ hours' boiling are desirable. The addition of dextrins to starch pastes is inclined to give a harsh 'boardy' 'finish,' but used alone good dextrin gives one of the softest 'finishes,' providing it is free from unchanged starch. Starch may be modified to leave it with most of its properties unchanged, with the exception of the viscosity, which is greatly reduced, thus allowing effects to be obtained similar to those given by non-starchy materials.

Many of the dressings commonly used contain two or more different kinds of starch, which are often mixed in the dry state and gelatinised together. It is considered preferable by some workers to gelatinise the different starches separately, afterwards mixing the pastes and boiling the mixture for a short time to obtain a homogeneous mass. In this way, a more uniform gelatinisation of the starch granules is obtained. In a mixture of two starches, dry-mixed before gelatinisation, there is always a danger that the granules of the starch swelling at the lower temperature will form a gelatinous coating around the granules bursting at a higher temperature, thus insulating them and preventing their gelling. Although such a paste may appear normal when used as a dressing, it has the tendency to 'dust off' after some time.

Wheat Flour.—Kuo-Chun Chin¹⁶ has examined samples of flour prepared with a silk bolter cloth and a metallic bolter and considers that the resulting flours have different properties which he ascribes to differences in particle size.

The method of preparing wheat-flour size is to steep the flour in water and allow fermentation to proceed. Various stages of fermentation may be distinguished, and the action stops when the ferments have used up all the available nutrient material, or are destroyed by the products of their own metabolism. Alcoholic fermentation takes place, and is followed by the formation of acetic and butyric acids, etc., the gluten and nitrogenous constituents also being attacked and solubilised. The suspension is generally acid when finished, and if coloured goods that will not withstand acid are to be 'finished,' the size is neutralised with an alkali such as ammonia. The odour from a vat containing fermenting materials is not unpleasant, but should a foul odour develop, the vat should be discharged and thoroughly cleaned out, otherwise the next batch will also be contaminated. This trouble is generally due to the use of diseased or poor-quality flour.

Wheat flour fermentation can be shortened considerably if about 0.25 per cent. of washing soda on the weight of flour is added to the vat and the mixing well stirred while fermentation proceeds. At the end of the fermentation period an antiseptic is added and the stock diluted and mixed for boiling.

When using wheat flour prepared by this fermentation method about twice as much flour is required on the weaving warps as would be required if sago or farina were used. The handle and appearance of the finished materials are similar and the wheaten size is quite readily removed. As more nitrogenous material is present in this case it is wise to add some fungicide to prevent the growth of mildew which grows more heavily on this type of size than on those made from straight starches.

Firmness and the impression of solidity are obtained by the use of *wheat starch*, which penetrates well, and by beetling or calendering gives a good glazed 'finish'. A mixed starch, however, is generally used in beetle finishing.

An interesting patent dealing with a use of starch in relation to textiles but rather unrelated to the foregoing covers the use of chlorinated starch in rayon spinning solutions. The fibres so produced have a low lustre which is still further decreased by after-treating the material with hot water.¹⁹

Various methods for evaluating starches for use on fabrics have been described by W. T. Schreiber and W. L. Stafford.²⁰

The methods described include those for judging starch mixtures from a processing or plant operating viewpoint and methods for evaluating the quality of starched fabrics. The stickiness of starch mixtures during ironing (see p. 289), and the penetration of such mixtures, are measured and the transparency of starch films, and the smoothness, stiffness and resistance to crushing of the starched fabrics, are determined. These methods may be used, with advantage, in evaluating other sizing and finishing agents and for full details readers are referred to the original paper.

Tinting and Blueing Agents.—To give the appearance of whiteness, blueing agents are often added to dressing for white goods, and soluble dyestuffs and pigments are sometimes added to the dressings for loaded coloured goods, especially if the ground colour is a heavy shade, in order to mask the whitish cast that would be given to the fabric by their use alone, so causing the dyeing to look 'bare'. Ultramarine is widely used for tinting white dressing, and the dressing should be neutral in reaction because traces of acid will cause the ultramarine to discolour to a grey or brown shade, and thus defeat its own purpose. The neutralisation may advantageously be carried out with ammonia and the presence of excess alkali is not harmful. Indigo Carmin and Paris Blue have also been used as blueing agents, but do not satisfy as many requirements of this work as does ultramarine. The amount of tinting agent employed depends on the particular effect desired by the 'finisher,' who makes the addition to suit his requirements.

The Suitability of Starches and Dextrins.—Starches from some sources contain sulphurous acid either in the free or combined state; when the free acid is present it is inclined to 'tender' goods that are stored in a warm place, so that freedom from this compound is desirable. In white dextrins the presence of unchanged starch should be looked for, because it alters the working properties and affects the type of 'finish' obtained, even when present in small quantities. Freedom from acids and glucose is also often desirable if discoloration of the finished goods on storage is to be avoided. Where neutral dressings are required it may be noted that some starches, such as maize and rice starch are very frequently alkaline in reaction, and the substitution of a portion of potato starch in a 'mix' by one of these starches sometimes serves to neutralise the remainder of the acid in the mixture. Fillers, e.g. talc, barium sulphate, and china clay, are also frequently acid, which splits any soap present in the dressing to produce fatty acids which, on oxidation, give rise to undesirable odour in the goods.

The Printing of Textiles.—The reproductions of colour patterns on textiles, other than by weaving, may broadly be referred to as 'printing'. The usual procedure is to add dye-stuffs, or their solutions, together with the required chemicals, to a paste prepared from starch, gum, albumin, or other substance which forms a mucilage with water or spirit.

These pastes are applied to the cloth in a variety of ways, by stencilling, by aerograph spraying, but chiefly by engraved rollers. The numerous requirements demanded of a thickener for printing are often contradictory, and each printer adopts the thickening which suits his own requirements.

For cotton, normal thickenings are used, but for other fibres, where wetting of the fibre is more difficult or other problems enter into the question, the natural gums are more generally used.

Function of the Thickener.—Thickenings may be divided into two classes, (a) those removed after printing, e.g. starches, British gums, vegetable gums; and (b) those used as fixatives and not removed after printing, e.g. casein and albumin. The thickener should serve for the following purposes:—

1. As carrier and diluent for the dyestuffs and chemicals required for developing or fixing the colour. It should, at the same time, prevent crystallisation or precipitation of the other ingredients both before and after printing the paste. The finer the dispersion of the dyestuff or the greater solubility in the colloidal thickener the better the results.

2. Provide a medium of such plasticity that will feed smoothly into the engraved portions of the roller, remain there until transferred to the cloth, and not spread along the fibres under the pressure of the printing process, or by capillary action, thus deforming the pattern.

3. Should delay chemical reaction between the constituents of the paste, e.g. a colour with its mordant, until the cloth is processed to bring about the reaction.

4. Should transfer completely from the rollers to the cloth.

5. Except where the thickening is used to fix the colour, e.g. printing with pigments, it should be easily removed on washing and so not alter the feel of the fabric.

6. Should be inert towards other constituents, non-hygroscopic, and cheap.

Colour Value.—The colour value obtained from printing a particular dyestuff depends, to some extent, upon the thickening agent employed, that having the lowest solid-content generally giving the best colour value. However, the colour value is

generally outweighed in importance by that of getting the right effect to produce a marketable product, irrespective of any economy of dye which is effected by varying the thickening.

Mucilages, such as locust bean gum and tragacanth, which give fairly thick mucilages at 2-8 per cent., generally give better colour value than those which have a high solid-content, e.g. alkaline gum or gum senegal. Good colour value may be a false estimate in practical work, as it often entails increased running costs and lowered efficiency. It must be remembered that in printing fabrics the aim is to get the right effect, and the cost of dyestuffs and thickeners compared with the value of the finished printed fabric is very low, especially in fine work, e.g. silks. For the sake of a small saving, several 'pieces' of material costing a considerable sum each may be spoilt.

Certain thickenings, e.g. those made from wheat starch, do not penetrate the fabric, and consequently the paste containing the colour lies on the surface, which receives all the colour present, and thus becomes intensely coloured. Compared with another thickening containing the same amount of dyestuff, and which penetrates, or 'strikes,' right through the material, and so transfers the colour to a much larger fibre area, wheat-starch thickeners appear to give good colour value, but only on one side of the fabric. If the second thickening is gum tragacanth, another factor comes into play. This thickening is generally made up with 4-5 per cent. of gum, whereas wheat-starch thickening contains about 12-15 per cent. of solid matter. When the two are printed the amount of solid matter present between the fibre and the colour particles farthest from the fibre is about three times as much for wheat starch as for gum tragacanth. The dyestuff has therefore farther to migrate to the fibre in the first case, and thus less dyestuff will be fixed in the same time of processing. The poor penetration of wheat-starch thickening, however, outweighs this disadvantage.

The colour-mixer and the foreman in a print works know by experience how and when to alter a thickening to suit different styles of work, and often do so automatically without being able to explain exactly why. The actual comparison of thickness, with regard to general utility, has to be carried out over long runs on a large scale, as laboratory or pilot plant trials are of very little use.

Starch Products used for Thickenings.—The value of a thickening depends largely on its viscosity, plasticity, and the percentage of solid matter in the solution at working strength.

Starch thickenings, or those made from printer's flour, are

usually prepared by pasting the materials to a sludge with water, adding more water and then 'boiling' the mass in a steam-jacketed pan with constant stirring. To prevent the mass sticking to the sides of the pan when heating, and to improve its working properties, it is customary in many print shops to add about a quarter of a pint of a vegetable or 'colour' oil to every gallon of the paste before boiling, the sides of the pan being rubbed with the oil and the rest added to the paste on charging. In some cases mineral lubricating oil is incorporated, but a saponifiable oil is preferable.

The keeping quality of neutral starch pastes is not high under normal conditions of storage, and is very greatly improved if a little acetic acid is added. All the usual precautions as to cleanliness of plant and elimination of contamination should be taken, and a good quality of starch should be used in preparing the thickenings. If these points are observed no trouble should be experienced, but should a batch become watery or 'go off,' the trouble cannot be rectified and the batch should be discarded.

Wheat starch has good, smooth-working properties, and at one time was probably the most widely used. Both it and maize starch are used at a concentration of about 12-15 per cent, i.e. 1-1½ lb. to the gallon. A mixture of maize and tapioca starches simulates the working properties of a wheat-starch thickening and has been used to replace this when the price of wheat starch was high. Maize-starch paste by itself lacks 'body,' and does not work as well or keep as well as wheat-starch paste, and thus is rarely used alone.

Tapioca starch gives a strong stringy paste which cannot be used alone. As stated above, it gives a good thickening when used in conjunction with maize starch.

Printer's or wheat flour is generally used, together with maize or tapioca starch, and, owing to its gluten-content, has a better holding or adhesive power than the starches. It is widely used as a thickening for alizarine-dyed 'styles' in which alumina and iron mordants are used, and it is stated to be the best thickener for use with azoic styles.

Disadvantages attendant on the Use of Starch Thickenings.

—Where an alkaline process is necessary to develop the colour, difficulty is experienced in using starch thickenings, the addition of caustic alkali causing them to form a rubbery mass, useless for printing. However, caustic alkalis can be incorporated into starch thickenings by pre-treating the dry starch with alkali of 90° Tw. and, after heating and constant stirring, diluting the mass with water to a workable consistency. Pastes made in this way

keep very well, and are used in some print works for printing indigo. Alkaline carbonates are often used, and here the same effect is to be noticed, but it is not so pronounced.

After printing and fixing the colour the thickening is often removed by washing the goods. Starch thickenings are not readily removed by washing, and impart a harsh feel to delicate fabrics. At one time a harsh or 'boardy' finish was in demand, but this demand has now decreased and smooth soft finishes are required, so that use cannot always be made of the excellent working qualities of starch thickenings.

Thickenings of British Gums.—As pointed out elsewhere (Chap. 6), a large range of British gums is on the market, and they are widely used for thickenings. They possess good working properties, and their stability to alkalis varies inversely with the content of unchanged starch. The availability of a wide range of these products renders easy the selection of one suitable for any particular type of work. British gums have the further advantage over starch in that they are readily and completely removable from the finished printed design, leaving the cloth with the required soft 'handle'.

Several grades of British gum are used in the printing trade, and vary from 'lightly calcined' gums to those which have been 'highly calcined'. A lightly calcined British gum may contain from 40-50 per cent. of unchanged starch, and would be used in thickenings at a concentration of about 20-30 per cent., the product being paste-like in consistency. Moderately calcined gums may be used with alkali carbonates, which do not cause much variation in their working properties, but they cannot be employed with caustic alkalis as the pastes obtained are unworkable on the machines.

Well-calcined gums can be used with both caustic carbonates and alkalis, as little or no unconverted starch is present; pastes made with them containing about 50 per cent. solid matter have a semi-fluid consistency.

A very highly-calcined gum, known as Senegal Gum Substitute, is used in silk printing, and is probably the last member of this group of products to be of practical value. It contains no starch and consists of a mixture of the lowest members of the family analogous to the dextrans. A workable paste, which penetrates well into the fabric, is obtained when a mucilage is prepared containing about 70 per cent. of solid matter.

The following recipes may serve as an indication of the type of starch and British-gums thickenings used in printing textiles: 350 pts. of wheat starch are suspended in a 1,000 pts. of water

and 1,000 pts. of an 8 per cent. gum-tragacanth mucilage are added. The mixture is boiled for half an hour with constant stirring, cooled and strained through a strong cotton cloth. A paste made in this way is much superior to that obtained by boiling the starch separately and then mixing with the gum-tragacanth mucilage, the paste being even and possessing smooth-working properties.

Thickenings for use with basic colours generally contain acetic acid, as the following typical recipe shows: 630 pts. of maize starch, 320 pts. tapioca starch, 4,000 pts. water, 2,000 pts. of an 8 per cent. gum-tragacanth mucilage, and 480 pts. of acetic acid (80 per cent.) are boiled together with constant stirring for 40 minutes. Before the mass is put in the pan, the sides are oiled, as previously mentioned, with 80 pts. of a vegetable oil (which is sometimes diluted with a little mineral oil for cheapness) to prevent the paste sticking to the sides and to improve the smoothness of working on the print machines.

Certain colours, such as vat dyestuffs, are reduced on the cloth to the leuco state during the processing which follows the actual printing, or in certain cases they may be reduced before printing. As the printing paste must be alkaline, thickeners stable to alkalis, such as British gums, are employed. The following illustrates the type of mixture used in such a thickening: 2,000 pts. of a moderately calcined British gum are boiled for 20-30 minutes in 3,600 pts. of water, and 1,670 pts. of potassium carbonate added, the mixture is boiled for a further 10 to 15 minutes and then allowed to cool. When cold 500 pts. of glycerine and 980 pts. of sodium formaldehyde-sulphoxylate are well mixed into the thickening.

J. Pokorny¹ gives a recipe for a thickening to be used for printing on cotton. It is made by boiling 145 pts. of a dextrin, 52 pts. of maize starch, 104 pts. tapioca starch and 2 pts. of stearic acid in 900 pts. of water, then adding 700 pts. of resorcinol. A considerable drop in temperature is observed when this addition is made, and the pasty appearances of the mass disappears on stirring. After 48 hours it becomes resinous or rubber-like and must therefore be used soon after being made up. The film produced by drying at 95-120° C. is claimed to be insoluble in alcohol, water, benzine, and ether.

Other starch derivatives on the market have a limited use for certain types of work. There are a number of patents covering the use of cellulose and starch derivatives for various purposes, but in the actual manufacturing processes cellulose is generally used in preference to starch to make the product which appears

on the market. Of these the so-called Colloresins are probably the best known¹⁰; they are cellulose compounds containing about 23 per cent. of the methoxyl group. Bayer² has covered the use of acetyl cellulose in admixture with boric or glycollic acid³ as a printing-paste thickener, the preparation and use of the products obtained by the action of ethylene oxide on starch, dextrin, gum tragacanth, etc., and of the water-soluble cellulose ethers which are suitable as thickeners.⁴⁻⁷

The printing of textile fabrics is an art, and there are a number of points which cannot as yet be rationally explained. Although work has been done recently to evaluate different properties of the printing paste,¹¹ and to co-ordinate them with the working properties of the paste when used in large-scale work, the results of these investigations are at present too immature to warrant detailed discussion. Rule-of-thumb methods still persist and adjustments to the printing pastes are made in an almost instinctive manner by the colour-mixer. However, despite our lack of scientific knowledge of the subject, many varied and very beautiful coloured effects are obtained.

REFERENCES

1. J. POKORNY, *Kunststoffe*, 1927, **17**, 31.
2. BAYER, G.P. 291,802.
3. — G. P. 292,589.
4. — G.P. 368,413.
5. I.G. FARBENIND., E.P. 279,864.
6. BAYER, G.P. 363,192.
7. I.G. FARBENIND., E.P. 359,618.
8. F. OHL, *Gel. Leim u. Klebs.*, 1928, **1**, 4138.
9. F. D. FARROW and E. JONES, *J. Text Inst.*, 1927, **18**, T1.
10. M. KERTH, *Textilber.*, 1937, **18**, 378.
11. S. N. GLARUM, *Amer. Dyest. Rep.*, 1934, **23**, 175; 1936, **25**, 150; 1937, **26**, 124, 437; 1938, **27**, 14, 308.
12. KALLE & CO., E.P. 399,998, 1933.
13. J. E. EVANS, *J. Soc. Dyers Col.*, 1933, **49**, 250.
14. F. D. FARROW and S. M. NEALE, *J. Text. Inst.*, 1925, **16**, T209.
15. M. S. FURRY, *U.S. Dept. Agric. Tech. Bull.*, No. 674, 1939.
16. KUO-CHUN CHIN, *Compt. rend.*, 1940, **210**, 581.
17. KALLE & CO., E.P. 521,468, 21/11/1938; G.P. 1 12 1937.
18. M. S. FURRY, *J. Home Econ.*, 1936, **28**, 687.
19. E.P. 443,060.
20. W. T. SCHREIBER and W. L. STAFFORD, *Ind. Eng. Chem. (Anal.)*, 1942, **14**, 227.

ADDITIONAL REFERENCES

- K. GEHARD, *Zeit. angew. Chem.*, 1909, **22**, 2484. (Lightfastness of dyestuffs decreased by starch but increased by dextrin in finishes.)
- S. R. TROTMAN, *J. Soc. Chem. Ind.*, 1911, **30**, 1294. (Loss of colour and tendering of fabrics may be due to faulty starch in the finish.)
- P. BEAN, *J. Text. Inst.*, 1915, **6**, 223. (Full discussion of various starches used in sizing.)

- W. R. CATHCART, *Text. World*, 1921, **59**, 2895. (Penetration of size into fabrics shown by photomicrographs.)
- W. B. NANSON, *Cotton*, 1921-22, **86**, 161, 243. (Notes a large fall in viscosity of potato-starch pastes on boiling.)
- G. SMITH, *Col. Trade J.*, 1921, **8**, 147. (General.)
- W. B. NANSON, *Cotton*, 1923, **87**, 661, 700, 721. (General.)
- W. R. CATHCART, *ibid.*, 1924, **88**, 818. (General. Sizing.)
- C. H. HARPER, *ibid.*, 1924, **88**, 265. (Glazing yarn. General.)
- W. B. NANSON, *ibid.*, 1924, **88**, 811, 1116, 1126; 1925, **89**, 354. (Textile printing. General.)
- W. A. NIVLING, *ibid.*, 1924, **88**, 800, 863. (Preservatives for sizes recommended. Size should be fluid when it reaches the last squeeze-rolls.)
- J. WOODMAN, *Text. Col.*, 1924, **46**, 717, 783; 1925, **47**, 232, 640, 736, 805. (Sizing value of starches discussed.)
- H. SEYDEL and A. H. REINERS, *Text. World*, 1925, **67**, 2986. (General. Sizing.)
- R. HART, *Amer. Dyest. Rep.*, 1936, **25**, 231. (Warp sizing.)
- P. L. MANN, *ibid.*, 1937, **26**, 177. (Recipes for sizing.)
- C. P. WALKER, *ibid.*, 1935, **24**, 374. (Use of Aktivin for solubilising starch.)
- L. F. GLEYSTEEN, *ibid.*, 1938, **27**, 14; *ibid.*, 1939, **28**, 280. (Printing thickeners.)
- J. E. EVANS, *J. Soc. Dyers Col.*, 1935, **51**, 319. (Desizing with enzymes.)
- G. F. DALENOORD, *ibid.*, 1932, **48**, 275. (Uses of starch in textile trades.)
- J. A. KIERNAN, *ibid.*, 1937, **53**, 379. (Printing thickeners.)
- A. MOLNAR, *Mell. Textilber.*, 1936, **17**, 234. (Enzymes for desizing.)
- KEHREN, *ibid.*, 1935, **16**, 875. (Enzymes for desizing.)
- V. P. SEYDEL, *Cotton*, 1936, **100**, 74, April. (Chemicals used in warp sizing.)
- J. WAKELIN, *Text. Col.*, 1938, **60**, 302. (Permanent finishes.)
- ANON, *Text. Manuf.*, 1937, **63**, 376. (Starches for finishing.)
- P. COLOMB, *T.I.B.A.*, 1937, **15**, 223. (General.)
- L. H. and J. FISHER, *Deutsch. Textilwirtschaft*, 1937, **4**, 11. (Detailed review of starch for textile work.)
- F. SICHEL, *Brit. Appl.*, 5584/38. (Cellulose-ether carboxylic acids as sizing agents.)
- SOC. POUR L'IND. CHIM., BALE, F.P. 809,932, 1937. (Urea-formaldehyde resins used with starch for sizing.)
- ULTRAZELL G.M.B.H., E.P. 472,473, 1936. (Fluorescent substances added to finishes to increase whiteness.)
- INTERN. PATS. CO., F.P. 819,374, 1937. (Halogenated starches as thickener in textile work.)
- I.C.I., E.P. 472,389, 1936. Equivalent to F.P. 816,387. (Fastness of starch improved by treatment at 90-140° C. with quaternary ammonium compounds.)
- PATENT CO. LTD., F.P. 810,688, 1937. (Diastase on hydrolytic products of starch used for sizing.)
- I.G. FARBENIND., Anm. I. 47,634, IVc/8k. (Treatment with chloral hydrate and urea to increase fastness of starch finishes to washing.)
- STEIN, HALL & Co., U.S.P. 2,083,982, 1936. (Urea, starch, and water for weighting textiles.)
- FIRMA ARNOLD H. WIVE, G.P. 647,997, 1937. (Laundry starch.)
- A. E. WILLIAMS, *Chem. Trade J.*, 1934, **94**, 190. (Starch for textile purpose.)
- J. A. CLARK, *Dyer*, 1934, **71**, 24. (General. Finishing.)
- F. OHL, *Spinn. u. Web.*, 1935, **53**, (26), 8. (Desizing.)
- ANON, *Textilber. (Eng. Ed.)*, 1930, 154. ('Quellin' described.)
- A. KOSEK, *ibid.*, 1935, **16**, 23. (Testing printing thickeners.)
- S. M. NEALE, *J. Text. Inst.*, 1927, **18**, T25. (Mill practice of heavy sizing.)
- F. KRONBERGS, *Latvij. Univ. Raksti.*, 1934, **2**, 385. (Surface tension and viscosity of printing thickeners.)
- LAUCKS, U.S.P. 2,098,083. (Urea-formaldehyde-resin starch as sizing agent.)
- E. PEZOLD, *Textilber.*, 1936, **17**, 222; 1938, **19**, 516. (Recipes for printing thickeners.)

- J. RIERE, *T.I.B.A.*, 1938, **16**, 321. (Identification of starches in finishes and thickeners.)
- JACOBY, *Amer. Dyest. Rep.*, 1938, **27**, 349. (Factors affecting colour value of print pastes.)
- DU PONT, U.S.P. 2,148,951. (Starch ethers and esters as printing thickeners.)
- E. M. MULLER, G.P. 671,259. (Printing thickeners.)
- E. V. PEZOLD, *Melliand. Textilber.*, 1938, **19**, 516, 593 and 743. (Comparison of newer textile printing thickeners.)
- I.G. FARBENIND, F.P. 766,119. (Formaldehyde on starch in presence of acid to give resistant finishes on textiles.)
- NORDDEUTSCHE KARTOFFELMEHL-FABRIK. M.B.H., G.P. 666,252, 1938. (Wetting agents dried into starch. Products used in textile industry.)
- G. S. RENSHAW, *Chem. Age*, 1939, **41**, 123. (Desizing with enzymes. General.)
- KLEBSTOFFWERKE, 'Collodin,' G.P. 414,979, 1922. (Sizes, by heating starch with alkali salts of weak organic acids which only dissociate and act at higher temperatures.)
- J. STRASCHNOW, E.P. 518,510. (Acid-roasted, powdered manioc root for printing thickeners.)
- A. E. WILLIAMS, *Text. Colourist*, 1939, **61**, 766. (General.)
- L. MAYER, *Textilber.*, 1940, **21**, 176. (Various types of amylases and their use in desizing discussed.)
- J. SÉNÉCHAL, *Rusta*, 1939, **14**, 333. (Various methods of testing starch to be used for sizing described.)
- J. S. PECKER, B.P. 624,426, 5 3 1946. (A liquid laundry starch containing pine oil, borax, 'blue', salt and starch claimed.)
- F. G. PIANA, U.S.P. 2,462,108. (Warp size of unusual strength and flexibility from mixture of maize, wheat or tapioca starches with waxy maize starch.)
- S. N. GLARUM and J. J. THOMAS, U.S.P. 2,400,820, 21/5/1946. Continuation of U.S.P. 2,302,310, 17/11/1942. (Starch pastes preserved for long periods by incorporating a water soluble carbamide-aldehyde addition or condensation product.)
- H. REHMANN, *Monats. Textil-ind.*, 1940, **55**, 38. (General. Sizing.)
- J. and J. TAKAMINE, U.S.P. 1,660,458, 28/2 1928; Appl. 17 12 1921. (Desizing with mould diastases.)
- L. MAYER, *Textilber.*, 1940, **21**, 176. (Desizing with amylases discussed.)
- J. PORZKY, *Z. ges. Text. Ind.*, 1936, **39**, 198. (Enzymes in desizing.)
- C. W. BENDIGO, *Textile World*, 1944, **94**, No. 6, 123. (Sweet potato starch in textile work.)
- S. DRAKE, U.S.P. 2,275,845. (Sizing and finishing compound of relatively constant fluidity by mixing cereal and tuber starches.)
- H. J. HENK, *Deut. Wollen-Gewerbe*, 1938, **70**, 1591. (Discussion of enzymes in desizing and their properties. Malt diastase preferred.)
- R. E. HOWELL, *Amer. Dyestuff Rep.*, 1937, **26**, 342. (Malt enzyme, acid-alkali and ammonium persulphate methods for desizing described and discussed.)
- ROHM and HAAS, U.S.P. 2,267,265. (Fixation of starch by phenolic methylene tertiary amine or its salt or quaternary salt.)
- M. F. POZDEEV, via *Khim. Referat. Zhur.*, 1940, No. 10-11, 107 and C.A. **37**, 1274. (Starch printing thickeners, preparation.)
- I. G. FARBENIND., E.P. 526,839. (Finishing agents and printing thickeners by hydrogenation of starch at 30 atmos. pressure for 15-20 hours in presence of nickel catalyst.)
- W. A. NIVLING, *Textile World*, 1924, **65**, 2999. (General.)

CHAPTER 13

MISCELLANEOUS USES

The Soap Industry.—The use of starch as a filler in soaps has been suggested often, and appears to be practised to a fair extent in South America. In Germany it has also received attention during the two world wars as a consequence of the national need for reducing the fats and oils in soap, minimising the blockades and finding an outlet for home-produced starch. It is known as a ‘Verschnitt’ agent,²¹ a term introduced by E. Jaeschke to indicate that it is neither an adulterant nor, strictly speaking, an improver. Some 50,000 tons of potato starch were consumed annually in Germany before the 1914-1918 war for this purpose; between the wars soluble starch was used.

Rice starch is added to toilet soaps in some countries, but in Germany potato starch, and in Guatemala, Yuquilla starch are used. Those who advocate the use of starch in soap give the maximum amount that can be added to most kinds of soap as 15 per cent., and they consider these concentrations harmless, except for white soaps, in which the inclusion of excess starch may affect the colour.²² The opponents of this suggestion point out that starch has little or no detergent properties, and therefore its inclusion is pure adulteration. On the other hand, the inclusion of starch does not appear to affect lathering, or indeed any other property, to a marked extent; in fact, some claim that the incorporation of starch in soap improves both the stability and volume of the lather.

Starch alone swells in water and forms an adhesive paste on heating, the colloidal solution having the protective action and strong adsorbent properties usually associated with long-chain organic colloids. There is, therefore, some ground for expecting starch to be innocuous to soap, even if it does not increase its detergent power.

In Germany the best grades of ordinary starch and flour are known as Hochfein, Superior, and Prima, in descending order of quality. These are of high gloss and maximum whiteness, free from chlorine and acid, and contain 0.25-0.5 per cent. of mineral matter. The moisture-content should not exceed 20 per cent. and not more than a trace of combined chlorine or iron should be

present. Kröner and Steinhoff²⁰ have elaborated another grade of starch, called by them 'Industrial Starch,' which, although indistinguishable from ordinary starch, has a lower ash-content of a different constitution; its physical properties are claimed to be somewhat out of the ordinary, enabling 25-30 per cent. of it to be incorporated in soap. The inclusion of 20 per cent. of this new starch was found to reduce the water-loss of a coconut-oil soap from 11·9 to 4·9 per cent. over four weeks. The authors also confirmed the claims for increase in lather number and stability of the lather.

In addition to those who criticise the inclusion of starch in soap because it is merely an adulterant without detergent power, other workers maintain that its inclusion is detrimental,²³⁻²⁴ especially if the soap is to be used to wash fabrics printed or dyed with vat colours, on the ground that these colours are reduced by the combined action of the starch and its by-products in the presence of the alkali. Such an action would render the dyestuff soluble and therefore loose to washing.

Some workers prefer the use of starch to that of sodium silicate. Kröner and Steinhoff²⁰ have shown that by heating starch for periods varying from $\frac{1}{2}$ hour to 12 hours in the presence of a 2 per cent. soap solution, either alone or with sodium silicate or soda lye, no measurable amounts of reducing substances were formed which could be detected by Ost's test or by Fehling's solution. Despite the elaborateness of the tests performed by these authors, further work on a large scale is needed before the matter can be settled, but the balance of evidence suggests that the inclusion of starch is practically harmless, and that it offers certain advantages which will not be overlooked by the trade, especially in view of the present world shortage of fats (see also W. Schültze¹²).

For toilet or milled soaps, the starch is added in powder form to the chips before milling. If desired, it can be used in the manufacture of soap flakes, but its use in soap powders is uneconomic, although it may not be so for shaving powders. The following example illustrates the composition of a shaving powder containing starch :—

Castile soap powder	800 pts.
Maize starch	200 "
Cassia oil	6 "
Caraway oil	1 pt.
Geranium oil	3 pts.

The powders are first mixed, the oils are added, and the whole thoroughly re-mixed.

A product which is claimed to have detergent properties is

prepared, according to A. L. Sodergreen,¹ by heating corn-flour to 120° C., or lower, in the presence of moisture to break down the protein matter and to hydrolyse the starch. The mixture is then made alkaline with caustic soda and reheated under pressure to saponify the oil present, any excess caustic soda being neutralised finally with carbon dioxide under pressure.

Although laundry work does not come under the heading of 'Soap Industry' it is convenient to mention here the use of starch in the laundry. For imparting a glaze, or as stiffening, rice starch is used in conjunction with waxes, e.g. paraffin wax, which are often added in the form of an emulsion. Soluble starch, dextrin or glucose all find use as the carrier and adhesive in the making of 'laundry blues,' a pigment like ultramarine being the actual tinting agent and imparting an apparent whiteness to the cloth.

Laundry Starches.—There has always been considerable reticence on the part of laundrymen, in common with textile finishers, on their use of starch. The final effect in both industries is largely influenced by the skill of the operative. Even using the same materials in ostensibly the same manner sensibly differing results are often observed. Since the housewife is largely influenced in her buying and laundering of textile fabrics by such factors as appearance and handle, the reason for a desire for secrecy becomes apparent. Nevertheless, it has been possible for suppliers to institute some measure of co-operative research, and the following brief résumé of the application of starch to laundry work has been written by Mr. J. M. Faulds.

For a considerable number of years rice starch was the most widely used material both for commercial and domestic work, despite its higher price. There are good reasons for its popularity although it must be stated that the cost of starch in a laundry is relatively unimportant. It has been found that the small granules of rice starch have a good penetrative power, besides imparting a good flexible glossy finish to the article. Furthermore, with personal linen it is more resistant to the effects of heat and perspiration from the body.

With the trend to less heavily filled fabrics, and a wider range of finishes, ideas on starching gradually modified. Again, the need for disposal of surplus quantities of other varieties of starch, including maize and wheat principally, led the makers of these to investigate their possible applications to the laundry industry. Various ingredients were added in endeavours to improve the natural qualities of the various starches, and the writer spent some considerable time in an experimental laundry plant investigating the use of these for laundry work.

It was found that practically all starches commonly occurring in practice could be used. With maize starch a characteristic 'boardy' feed was usually obtained; whilst wheat starch gave rather a soft effect. Blendings of these two were then tried with very good results.

In view of the trend towards adding the starch to the washing machine after the final rinse, and the importance of the degree of gelatinisation achieved on calendering, particular attention was paid to this procedure. It was found that, contrary to general supposition, only a fraction of the granules were burst when heat was applied, and this was found to apply even when the starch paste was prepared in a boiler. The behaviour of soluble starches and dextrans was investigated and it was found that some of these gave very pleasing results, which is understandable in view of the large use of these types of starch derivatives in textile finishing. In general the modified forms of starch have lower gelatinisation temperature ranges, and possess greater penetrating power, the latter property imparting a fullness to the article.

The practice of adding dry starch to the washing machine is rather wasteful as an appreciable quantity is lost when the water is run off. Further, it is not at all certain that each article picks up starch in its rumpled state uniformly. The use of wetting agents is often beneficial.

The addition of borax to laundry starches has always been largely favoured and undoubtedly is responsible for a considerable improvement in the results obtained. The quantity added may vary within the limits of 1-17 per cent. on the weight of starch, depending on the other constituents present. The mechanism of the action of borax on starch is as yet unknown but work is proceeding to elucidate the matter. Starch-borax compositions are often designated as 'gloss starch,' although trade descriptions seldom give accurate indications of composition.

Other mineral additions to laundry starches include china clay, chalk and some of the other filling materials commonly used in textile finishing. These may be added with a view to making good any large loss in weight during washing. This loss is not experienced to anything like the same extent with linen as with cotton, and even in the case of the latter the modern tendency is towards pure finishes. If such a mixture be used, the starch should bind in the filler which should not dust off on rubbing the laundered fabric. These fillers are always very much cheaper than starch and a buyer can be guided by an analysis of the ash-content of a brand under consideration.

The last type of addition to be considered is that of fatty matter. The choice often consists of tallow or stearin. A very pleasing effect results from the use of either of these two substances. One point deserving special attention is that of temperature. The melting-point of tallow and of stearin are both below the gelatinisation temperature range of commercial starches. Consequently, if the iron or calender is sufficiently hot to secure even partial gelatinisation some harm may be caused through melting and darkening the fatty matter present. The use of modified starches enables lower temperatures to be used on the calender and the difficulty is largely removed. If dry starching is used there is a tendency for the fatty matter to separate from the starch if the two have simply been dry mixed in manufacture. Even although an emulsion of the fat is added to an agitated suspension of the starch the two are found to separate during casting. It has been found possible, however, to incorporate the fatty matter with the starch in such a manner that when the mixture is thrown over the cage in the washing machine there is uniform dispersion and pick-up by the articles.

Finally, a word should be said about what is termed 'sticking'. This trouble is due to excessive starch being left by the articles on entering the calender on the lip of the machine where pasting and drying of the starch take place to be followed by charring. The brownish flakes peel off and become attached to subsequent articles. It must be borne in mind that all starches exhibit this tendency which can, however, be reduced. The most effective method of prevention is to fit squeeze rollers to remove surplus starch, before the heated bed is encountered. There has been considerable controversy over this subject and much work remains to be done. Undoubtedly routine practices in a laundry are largely responsible for the degree of trouble experienced from this source.

Cosmetic and Pharmaceutical Uses.—The use of wheat, maize and rice starch is specified in the British Pharmacopœia and that of maize starch in the American Pharmacopœia. Starch is used as a diluent and carrier in many of the toilet powders of to-day, e.g. the so-called Violet Powders, which consist essentially of perfumed starch powders, deodorant powders (*v.i.*) containing salicylic acid, boric acid or alum, and dusting powders containing zinc oxide, salicylic acid and starch.

In making these toilet powders care should be taken to ensure that the starch is perfectly dry before mixing. A basis of rice starch is widely used and is considered better than wheat starch, which has a bluish-white tone, or potato starch, in which the

granules are so large that the powder has a coarse appearance. A further drawback to the use of potato starch as compared with rice starch is the high gloss and inferior colour it imparts, but it is sometimes used for cheap goods.

In the manufacture of face powders, starch finds itself in competition with a number of other substances. The best face powders contain 50 per cent. or more of rice starch to which maize starch is often added in the manufacture of cheaper products. The question whether it is preferable to use starch instead of other carriers in face powders is debatable. Some medical men claim that starch may be rendered acid by contact with perspiration; also that when it works into the pores, the acid and moisture in the perspiration cause the small granules to swell. This swelling enlarges the pores, thus coarsening the skin and rendering the penetration of larger granules easier on subsequent applications. To overcome this alleged defect one manufacturer first heats the starch with water to swell the granules, and then, after drying, grinds the mass to reduce it to a fine powder, at the same time incorporating a wax to increase the water resistance of the powder. By this method he claims to produce a powder with satisfactory properties. It may be pointed out, however, to those who oppose the use of starch on the grounds stated above, that the powder is invariably applied in a thin layer, and is washed off and renewed after a relatively short contact with the skin, so that the part played by starch in beauty skin-treatments is not a harmful one. The mineral vehicles employed, such as talc, zinc oxide, magnesium or calcium carbonate, kaolin or kieselguhr, and the stearates of zinc and magnesium, are also open to the same objection, viz. that they may stop up the pores of the skin, although, of course, they do not swell in contact with water. A formula for a compressed tablet or 'compact' is as follows: rice starch 250 pts., talc 450 pts., china clay 250 pts., zinc white 50 pts., are well mixed together with a very small amount of binder, such as gum senegal or gum-arabic, and then compressed. The starch itself can sometimes be used as the binder, e.g. for certain medicinal tablets to be mentioned below.

Starches are rarely, if ever, put into infant powders or perspiration powders, although E. Donath² uses starch among other carriers for such powders. The powders claimed by Donath contain amylolytic or proteolytic enzymes, such as pepsin, pancrease, and urease, together with water-soluble compounds which are claimed to activate the enzymes in the presence of water, e.g. boric acid, sodium benzoate or salicylate. In making nursery powders, Donath uses enzymes which are activated by

compounds having an alkaline reaction in water, e.g. sodium salicylate.

Creams and mucilages are often made up on a base of glycerine and starch, or glycerate of starch. According to the preparation in the British Pharmacopœia, 20 gm. of starch, 130 c.c. of glycerol, and 130 c.c. of water are heated with constant stirring until a translucent jelly is obtained. This mucilage gives relief when applied to chapped hands or chilblains, and is used in admixture with zinc oxide as a cosmetic. Glycamyl or Plasma are other names by which glycerate of starch is known.

J. B. Termansen³⁹ has discussed the use of starches from various sources in various pharmaceutical preparations. When gelatine is also used in the same mixture 'coazervation' may occur leading to a slight separation of gelatine. He gives directions for the preparation of mixtures of bismuth salicylate, bromisovalin and salol with starch mucilage and the trituration of camphor by its aid.

Starch serves two distinct purposes in the making of pills: it is used as a coating and dusting agent, and as a binder for the materials of which the pill is composed. The pills may be coated with a mixture of syrup and starch paste and then rolled in a mixture of powdered starch and sugar. As a binding agent it sometimes appears in grey pills or in phenolphthalein pills. In the manufacture of aspirin tablets starch is used for a specific purpose: it is dried until as little moisture as possible remains, mixed with the acetylsalicylic acid and other components, and the mixture compressed into tablets. When the tablet is swallowed, the starch rapidly absorbs moisture and swells, thus setting up an internal stress which causes the tablet to disintegrate completely. San-Gri-Na, which is a proprietary remedy for obesity, is stated to contain 11 per cent. arrowroot starch, a vegetable extract, and phenolphthalein.

C. W. Bice and M. M. MacMasters⁵¹ use the property of some starches, of yielding an absorbent sponge when their pastes are frozen, to obtain soft, pliable and absorbent surgical dressing for internal use which is slowly absorbed by the body.

Instead of using starch iodide for treating wounds (see Vol. I), certain preparations of formaldehyde and starch, known as Amyloform and Euformol, can be used. The latter is a dextrin-formaldehyde product. Both substances are also sold for the treatment of colds.

Certain insect powders, such as beetle powders, sometimes contain starch as the carrier for the borax, sodium chloride, or other effective agent.

Starch has sometimes been suggested for, and used in, the making of depilatories, maize or potato starch being used instead of talc or other inorganic carriers for the metallic sulphide, which is the effective agent; it has, however, the disadvantage that it forms stodgy masses on the addition of water and sulphide, so that it is preferable to use a lighter grade of magnesium carbonate as the carrier.

Horticultural Uses.—Insect powders have already been mentioned, and in addition, starch or dextrin are sometimes used in the preparation of horticultural sprays. These sprays contain a killing agent for pests or fungi, together with a substance to cause the solution to penetrate cracks or spread over the leaves which, normally, are not easily wetted. Soluble starch, or more usually a yellow dextrin, is added to make the dissolved material adhere to the treated portions when the liquid medium evaporates. Although some people have used the feeble wetting-out properties of the dextrin to cause the liquid to spread effectively, and have tried to dispense with the use of a synthetic wetting agent, it is decidedly preferable to include the latter. In emulsions containing soap, the emulsifying agent also acts as wetting agent, and the sole function of the dextrin is that of an adhesive.

Fire-Proofing Preparations.—To obtain non-inflammable fabrics, J. Benoid³ used a maize or rice-starch sizing containing sodium tungstate, magnesium carbonate and sulphate, together with several other ingredients usually used in fire-proofing. H. Becker⁴ uses ammonium salts and aluminium sulphate in a starch preparation for the same purpose, whilst still another preparation⁵ containing talc, sodium hyposulphite, sodium chloride, and borax has also been suggested. According to H. J. Henk,³² starch for certain purposes can be fire-proofed with various mixtures of aluminium and ammonium salts containing borax. The use of certain metallic salts of starch for mildew-proofing has been claimed.⁵³

Explosives and Fuels.—Rice starch has been used as a crystallising and binding agent in moulded Black Powder explosives.⁶ Abelite is said to contain starch, ammonium nitrate, T.N.T. and sodium chloride; Ammonia Dynamite Pulverent, 20 per cent. nitroglycerine, ammonium nitrate, sodium nitrate and 19 per cent. rice starch or flour; whilst Ammonia Dynamite (French) is said to contain wheat starch. Bobbinite, a type of gunpowder, contains starch and paraffin wax. The different varieties of Carbonites, which are used in coal mines for blasting, contain wheat or rice starch; Foerdite and Fractonite contain 4 per cent. dextrin, and Gesilit Nos. 1 and 2 are said to contain 39 and 21 per

cent. of dextrin, respectively. Fulgurite contains 40 per cent. of wheat flour, and Gelatinwetterastralite 8 per cent. of potato starch. The explosive properties of nitro-starch are well known (see Vol. I).

According to A. Schrimppff³³ two kinds of nitro-starch explosives are used in America. For one kind, nitro-starch is mixed with sodium nitrate and an oil, a typical composition consisting of 50 per cent. nitro-starch, 47.5 per cent. sodium nitrate, impregnating oil 1.5 per cent. and sodium bicarbonate 1.0 per cent. This mixture has a high brisance and is readily detonated, making it suitable for chamber blasts and quarrying limestone or granite. The other type contains a large amount of ammonium nitrate mixed with the nitro-starch together with oxidisable materials such as T.N.T., coal dust and aluminium powder, together with a little oil. Explosives of this type have a lower brisance and are more difficult to detonate; they also give rise to larger amounts of gaseous products. Some of these mixtures are used in fiery mines. Investigations made at the Pittsburg experimental station on the sensitising of ammonium nitrate by nitro-starch are described by this worker (see also J. B. Bronstein¹²).

A similar demolition explosive containing barium nitrate, nitro-starch, coal dust, aluminium powder and dicyanodiamide has been described by W. O. Snelling.⁴²

C. H. Carey⁴¹ obtains an explosive by mixing starch and a granular water-soluble nitrate, of which at least 60 per cent. is ammonium nitrate, which may be coated in the usual manner with petroleum or paraffin, with water to a plastic consistency. The starch is modified by the nitrates and on drying the nitrate granules are firmly bound together by a thin film of starch.

Rice starch finds some outlet as a binding agent in the manufacture of match-heads,⁹ and has also been used in the manufacture of fireworks. In match manufacture the most important adhesive used to bind the chemicals forming the tip is a good grade hide glue, but starches and dextrans are also of importance. Not only do they function as adhesives, thereby reducing the amount of the more expensive hide glue, but they also act as thickeners and fillers which are readily oxidised and take part in the combustion when the match is struck. In most cases a satisfactory amount of starch or dextrin pastes to add to the mix is about 13-14 per cent. on the batch volume. Dextrans are considered to be better than starch for this purpose by a number of match-makers but, they are, of course, more expensive.

A further use for rice and other starches⁷ is to stabilise the colloidal catalysts used in the hydration of olefines, and to stabilise

coal-dust suspensions in oils that contain combustion catalysts and are used for fuel oils.⁸

Spent water from coal-washing contains very finely divided coal dust that is difficult to separate from suspended clay and other impurities, but the filtration and removal is facilitated by the addition of starch, which flocculates the particles and carries them down with it as it settles. By suitable selection of equipment, this method has been found practicable and effective for full-scale work. The starch for this work is often modified with zinc chloride and its efficiency is greatly increased by carrying out the precipitation under alkaline conditions. The well-known 'Unifloc Process,' for example, embodies the use of lime as the alkali (*v.i.*).

Both gelatinised starch and commercially prepared starch have been found to be effective in increasing the efficiency of high temperature filtrations carried out on salt water to remove mud, and it has been suggested that the use of a preservative is advantageous in assisting the starch to retain its efficiency in this type of process.⁴³ An interesting point is the use of starch for obtaining exactly the opposite effect to that just described in that starch is being used in increasing quantities in order to prevent the various constituents in the mud from settling whilst a well is being drilled.⁴⁴

N. V. de Bataafsche Petroleum Maatsch⁴⁷ in using starch in drilling muds to plaster the walls of the hole to prevent infiltration find heating the mixture to 70° improves its effect. G. E. Cannon⁴⁸ suggests the use of a starch ester of an aliphatic acid of low molecular weight for the same purpose. R. V. Andes and N. C. Ludwig⁵² use oxidised starch to reduce the viscosity of Portland cement slurries and to allow control of the setting time over a wide range.

L. Marton¹⁰ proposes to utilise waste coal dust in the manufacture of fuel briquettes in which the particles are cemented together, using starch. Such briquettes, however, suffer from the drawback of disintegrating when they become damp, and to overcome this, it has been suggested to use skimmed milk and to treat the briquettes subsequently with formaldehyde.

Some Unclassified Uses.—It remains to consider some isolated uses of starch in a few widely different industries. Starch is used as a dusting powder for moulds in foundry work and has been used in oilcloth manufacture, and as dispersing agent for vinyl acetate in hydrogen peroxide in making emulsion polymers.⁵⁰ A dimethyl derivative of starch has found use as a creaming agent for rubber-latex creaming,¹⁴ whilst according to another

patent,¹⁵ the backs of carpets may be finished with an aqueous, compounded, rubber-dispersion containing more unpeptised starch than rubber. It is also used as a dusting agent to eliminate tackiness in certain rubber articles, such as mackintoshes.

In conjunction with soap bark, the use of rice starch has been claimed¹⁶ for the manufacture of porous building blocks from hydraulic cement (see also K. Schenkel³¹); and a further use, of interest to the building engineer, is that for making bitumen and tar emulsions, in which it acts as the emulsifying agent.¹⁷

A 6 per cent. suspension of starch in a 40 per cent. alkali carbonate solution has been claimed as a plasticising agent for incorporation in finely divided cement material.³⁸

A. V. Petrov¹⁸ has examined the use of starch for speeding up the separation of the sludge formed in the manufacture of caustic soda by the lime process. He claims that the addition of 0.01 per cent. of starch increases the speed at which the carbonate formed in the process settles in the tanks. J. O. Samuel³⁴ produces starch gels for flocculating suspended matter by agitating modified starch at 70° C. with a concentrated aqueous solution of a neutral hydrated metallic salt, e.g. zinc, calcium, magnesium or lithium chloride or a thiocyanate until a thick gummy mass is obtained.

For the lubrication of stopcocks where ordinary fat solvents are in use, e.g. ether or light petroleum, a mixture made by heating 9 gm. of soluble starch in 22 gm. of glycerol at 140° C. until a homogeneous gel is obtained has been recommended⁴⁰ and found to be very effective by the author. When cold the product has the consistency of a heavy grease.

The U.S. Navy Standard Boiler Compound—used for softening boiler feed-water—consists of 76 per cent. soda ash, 10 per cent. trisodium phosphate, 1 per cent. starch or dextrin and 11 per cent. water together with sufficient cutch to yield 2 per cent. tannic acid.

Starch finds occasional use in the leather industry for finishing such leathers as sole leathers and the grain side of wax kips.

In the common electric dry-battery cell starch is used for several purposes. The label may be surfaced with starch and affixed to the battery with an amylaceous adhesive; the paper used for lining the walls of the cell may be coated with rice starch that has been treated with ammonium chloride and zinc chloride¹⁹; and the electrolyte in these cells may be carried in a mucilage, of which a rice-starch paste may form the basis. The Industrial Research Bureau of the Indian Government have recently found that the starch content of the electrolyte in dry cells can be

reduced considerably without any adverse effects. W. D. Staley and A. J. Helfrecht²⁹ have studied the gelatinisation of maize starch in dry cell electrolytes. A mixture of 2 pts. of starch and 1 pt. of corn meal was added to solutions of zinc chloride or of zinc and ammonium chlorides at 10° C. and after thorough mixing the time taken to gelatinise at 18° C. was determined. With 35 gm. of the cereal in 80 c.c. of zinc chloride solution no gelatinisation takes place unless the zinc chloride concentration reaches 35 per cent. The setting time decreases to a minimum as the concentration of zinc chloride is increased to 42 per cent. and then increases rapidly above this concentration. Ammonium chloride is less effective in promoting swelling, and similar results to those above are obtained with solutions in which some zinc chloride is replaced by ammonium chloride. They recommend making two solutions, one containing most of the zinc but little of the ammonium chloride and the other containing most of the ammonium chloride, a little zinc chloride and all the cereal and then mixing in suitable proportions to give a solution which will set in a convenient time for the preparation of dry cells.

The effect of the purity of the starch on dry cell performance has been studied by D. Venkateswarlu⁴⁹ who found starches containing 16 and 0.5 per cent. non-starchy matter, respectively, to give cells showing initial voltages of 1.55 and 1.55; to produce current at 5.2 and 6.5 amp., and to operate continuously for 6.5 and 9.75 hours, respectively, before the voltage dropped to 0.6.

Certain foodstuffs, such as eggs, oranges, and meat, are often stamped or marked to designate their grade or origin; and sacks, used for packing many substances are stamped or stencilled for a like purpose. Many of the marking inks on sale for this purpose consist primarily of an aqueous solution of a dyestuff to which is often added a yellow dextrin or thin-boiling starch to act both as thickener and adhesive.

An interesting use of rice starch is in the manufacture of luminous paints. Very pure starting-materials are required to produce the finer grade of product, and the presence of a minute amount of impurities often alters the colour or the intensity of the luminescence. Sulphides of heavy metals form the basis of many of these luminescent products, in the preparation of which certain metallic compounds are heated with starch. The starch acts as a reducing agent, and rice starch is generally preferred to potato starch because it is less likely to contain traces of iron compounds, which would adversely affect the quality of the luminescence. Anhydrous starch has been suggested for use for preparing fillers and thickeners in paints, lacquers and polishing

compositions.³⁵ The dehydrated starch is used to adsorb a water-immiscible liquid such as propylene dichloride and then mixed with a strong swelling agent. Ethers and esters of starch are coming into consideration as lacquer vehicles as has already been discussed (see Vol. I). Mention may be made here, however, of the fact that nitro-starch appears favoured for this work and the various patents (e.g. Ref. 45) have been reviewed by A. Kraus,⁴⁶ but allyl starch has also been found useful recently. S. E. Stockman³⁶ suggests the use of corn starch in glazing liquids to prevent running and for use in various woodfillers. Air-dried starch heated with formaldehyde in the absence of air until the mass no longer gives a blue colour with iodine is claimed³⁷ to give a product which can be moulded at high temperatures to a transparent body.

M. M. Nurkass³⁰ claims that printing rollers of outstanding durability can be made from 25 pts. starch and 25-30 pts. of magnesium-glycerine syrup. This syrup consists of 11 pts. of glycerine and 1.6 pts. of magnesium chloride. After filtering the starch-syrup mix and allowing to stand for 24 hours it is cast into moulds. The hardness of these rollers are said to decrease as the syrup-content is increased.

Starch has found use, during the war years, in the preparation of sintered porous metal parts. The starch for this purpose must be of uniform and small granule size, contain the minimum of ash and readily burn away.

Sorbitol is now made by simultaneous hydrolysis and hydrogenation of starch or dextrin using a nickel catalyst and pressures of approximately 100 atmospheres. The presence of certain metallic salts, e.g. magnesium, nickel or calcium chloride improves the efficiency of the conversion.¹⁰

REFERENCES

1. A. L. SODERGREEN, U.S.P., 2,049,476, 4/8/1936.
2. E. DONATH, E.P. 378,888.
3. J. BENOID, E.P., 14,205, 1906.
4. B. BECKER, E.P. 20,460, 1906.
5. A. J. JARMAN, *Scientific American*, 1910, 103, 364.
6. U.S.P., 1,913,344.
7. E.P. 413,043.
8. E. P. 408,951.
9. U.S.P. 1,831,760.
10. N. V. DE BATAAFSCHE PETROLEUM MAATS., Dutch P. 64,717, 15/11/1949.
11. L. MARTON, E.P. 21,755, 1904.
12. W. SCHÜLTZE, *Fette u. Seifen*, 1938, 45, 522.
13. J. B. BRONSTEIN (to Trojan Powder Co.), U.S.P. 2,170,629.
14. RUBBER PRODS. RES. ASS., E.P. 437,758.
15. ANM. I. 50,012, IVc/8k (3).

16. U.S.P. 1,937,472.
17. E.P. 387,657. (Lapsed.)
18. A. V. PETROV, *J. Appl. Chem. U.S.S.R.*, 1936, **9**, 34; *via Chem. Abst.*, 1936, **30**, 6140.
19. U.S.P. 1,911,400.
20. KRÖNER and STEINHOFF, *Seifens. Zeit.*, 1936, **63**, 272.
21. G. KNIGGE, 'Soap, Perf., Cosmetics,' 1936, 316.
22. H. NITSCHKE, *Seifens. Zeit.*, 1935, **62**, 840.
23. K. KIEFER, *ibid.*, 1936, **63**, 413.
24. K. L. WEBER, *ibid.*, 1936, **63**, 189.
25. P. BRETTSCHEIDER, *ibid.*, 1936, **63**, 311.
26. K. M. GAVER, U.S.P. 2,397,732, 2/4/1946.
27. N. I. KOZINE, *Maslob, Jir, Delo*, 1937, **13**, 28 (3); *Chim. et. Ind.*, 1938, **40**, 975.
28. L. ZAKARIAS, *ibid.*, 1936, **36**, 1095; *Chem. Trade J.*, 1937, p. 27. (Starch solutions for metal degreasing.)
29. W. D. STALEY and A. J. HELFRECHT, *Amer. Electrochem. Soc.*, 1928, **53**, April.
30. M. M. NURKASS, *Polygraphic Ind. (U.R.S.S.)*, 1939, No. 6, 44.
31. K. SCHENKEL, E.P. 285,470, 25/11/1927.
32. H. J. HENK, *Seifensieder-Ztg.*, 1939, **66**, 141.
33. A. SCHRIMPF, *Zeit. ges. Schiess- u. Sprengstoffw.*, 1930, **25**, 273.
34. J. O. SAMUEL and UNIFLOC REAGENTS LTD., E.P. 516,294, 29/6/1938.
35. U.S.P. 2,165,834, 1939.
36. S. E. STOCKMAN, *Amer. Painter and Dec.*, 1939, **16**, No. 6, 25.
37. SCHOLTEN'S AARDAPPEL MEELFABR., Dutch P. 46,185; *Chem. Zentr.*, 1940, **111**, I, 142.
38. HON. ADVISORY COUNCIL SCI. IND. RES., B.P. 521,293, 17/5/1939.
39. J. B. TERMANSEN, *Farm. Tids.*, 1943, **53**, 755,773.
40. B. L. HERRINGTON and M. P. STARR, *Ind. Eng. Chem. Anal.*, 1942, **14**, 62.
41. C. H. CAREY, U.S.P. 2,333,637.
42. W. O. SNELLING, U.S.P. 2,333,275.
43. F. PERKINS and B. C. CRAFT, *Amer. Inst. Mining Met. Eng., Tech. Publ. No.* 1551, 1943.
44. ANON., *Ind. Eng. Chem. Anal.*, 1940, **12**, 748.
45. W. D. BAWLBY (to Trojan Powder Co.), U.S.P. 2,261,642.
46. A. KRAUS, *Z. ges. Schiess- u. Sprengstoffw. Nitrocell.*, 1943, **38**, 170.
47. N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, Dutch P. 52,668, 15/6/1942.
48. G. E. CANNON, U.S.P. 2,417,235, 11/3/1947.
49. D. VENKATESWARLU, *Current Sci.*, 1946, **15**, 46.
50. I.C.I. LTD., B.P. 580,020, 23/8/1946.
51. C. W. BICE and M. M. MACMASTERS, U.S.P. 2,423,475, 8/7/1947.
52. R. V. ANDES and N. C. LUDWIG, U.S.P. 2,429,211, 21/10/1947.

ADDITIONAL REFERENCES

- J. SERBERLICH, *Modern Plastics*, 1941, **18**, No. 7, 64 and 98. (Use of starch in film-forming compositions and plastics reviewed.)
- J. F. WALSH and F. C. MILLER, U.S.P. 2,350,658, 1944. (Thin boiling starch, titanium dioxide, borax and salt as laundry starch.)
- C. REICHKE, G.P. 717,273, 1942 (40 per cent. potato starch with borax swelling starch, dextrose and swelling agent, e.g. urea. Ger.P. 726,979, 1942.) Addn. to above. (Borax replaced by alkali sulphates, magnesium sulphate or double sulphates of these metals.)
- R. A. VAN LINGE, Dutch P. 56,721, 15/7/1944. (Starch, formaldehyde, lactic acid and urea mixture autoclaved to give a press powder.)
- W. L. CRAIG, U.S.P. 2,425,058, 5/8/1947. (Mixtures of titanium dioxide and calcium starch metaborate as pigments for paper and paints.)

CHAPTER 14

UTILISATION OF THE BY-PRODUCTS OF STARCH MANUFACTURE

BY-PRODUCTS are obtained in the manufacture of the different varieties of starch, and some of them present the problem of their disposal ; others, on the other hand, may be commercially valuable and be worth recovering.

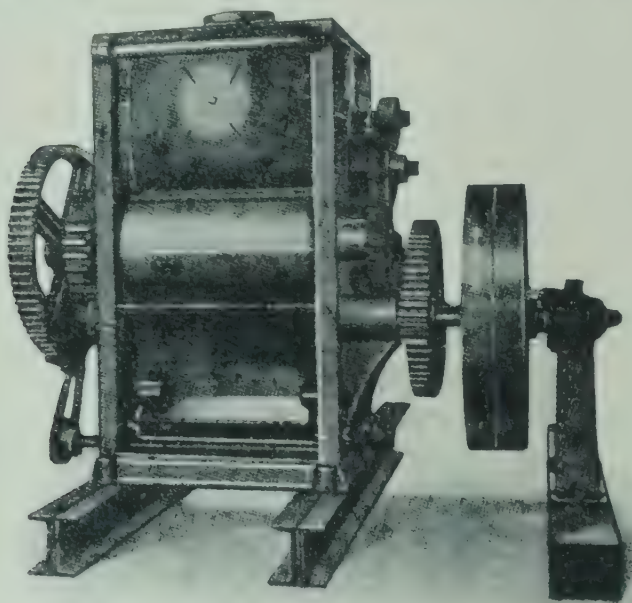
The by-products obtained in the manufacture of maize starch (see Chap. 3) are cattle-food, consisting of dried gluten, corn-bran and germ-oil meal, and corn-oil. The last-named is obtained in a yield of about 2·5-3 per cent. on the weight of the maize processed, and is used in several industries where a semi-drying oil is required. Steeping-water from the preliminary washing contains mineral salts and water-soluble proteins, and after concentrating from approximately 5-18° Bé., it is sprayed on the cattle-food whilst this is drying. In some cases it is still further evaporated and used as a nutrient medium for yeast and bacterial cultures, or for purposes where a non-coagulable water-soluble protein is required. The soluble products from the steep-water are removed by W. Sage¹ by precipitation with lime, transferring the liquor to a settlement tank, and after expressing surplus liquid from the sediment, drying the pressed product.

The maize gluten has a number of interesting possible uses in industry, and several grades are available commercially. One grade is known as carbohydrate-free, another grade is free from both carbohydrates and from the portion which is soluble in aqueous alcohol, whilst the third grade consists of the portion soluble in aqueous alcohol, the so-called 'Zein'.

The carbohydrate-free gluten is also produced in several grades, e.g. an oil-free grade, a bleached grade, and an oil-free and bleached grade. The various grades differ slightly from one another, but as a group their chief interest lies in their value as fillers or bases for plastics. They can be incorporated with both natural and synthetic resins or with cellulose derivatives, and are, in general, light in colour and thermoplastic. They react with formaldehyde or phenol, and if free from the portion soluble in aqueous alcohol are almost completely dispersed in dilute alkaline solutions. The percentage composition of the carbohydrate and

oil-free protein is approximately as follows : moisture 11, protein 76, ash 1.2, fibre 4, oil 1.1, starch nil ; the alcohol-soluble portion amounts to about 36 per cent.

The fraction which claimed early attention because of its solubility in aqueous alcohol—the zein—was isolated by Gorham in 1821. It is available only as a by-product of corn processing, and its potential yield is 1 lb. per bushel of corn. The commercial product contains⁶ about 90 per cent. of matter soluble in 80 per cent. alcohol, 8 per cent. moisture, 0.4 per cent. ash, and 0.4-0.6 per cent. oil ; it is marketed as a white, tasteless,



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FIG. 14:1.—A pulp-pressing machine.

odourless, amorphous solid. It is said to be resistant to light, is thermoplastic, has a high electrical insulating value, and is non-inflammable. It is unaffected by anhydrous alcohols or by organic solvents in general, whilst dilute acids and weak alkalis do not dissolve it. Solutions, can, however, be obtained with aqueous alcohols, dilute solutions of strong alkalis, molten phenol, or strong solutions of urea. It is also claimed⁶ to be compatible with many cellulose derivatives, plasticisers, natural and synthetic resins, and can be used in the preparation of stable glass-like plastics. Modifications are also used as adhesives and in the preparation of coating compositions for paper, etc., and this field is receiving some attention in the U.S.A.

E. Bartow and W. W. Walker⁹ have discussed the recovery

of compounds from corn starch steep-water and consider it a very likely source of inositol.

The by-products from wheat-starch manufacture are gluten and, as in the case of every other starch, waste water containing soluble and colloidal impurities. The disposal or utilisation of waste water is important in every starch factory, and various processes have been put forward for its use. One early suggestion²⁻³ was that it should be pumped on to meadow-land, like the effluents from sewage farms. An artificial manure was obtained by G. de Claubry,⁴ who treated the effluent with milk of lime and a tannin solution. Precipitation with lime was also used by Markl.⁵

By far the most important by-product from wheat-starch manufacture is gluten, which is used in preparing diabetic foods, speciality breads, for feeding cattle, sometimes as a thickening agent in textile printing, and as a size or adhesive. The gluten for technical purposes is largely supplied from the factories operating the Martin process, whereas that for food uses is generally obtained by the Fesca process, which yields a product containing all the non-starchy matter in the wheat. As moist gluten tends to decompose after a day or two, it must be dried before it is stored. Fermentation under controlled conditions gives a size which is without any offensive odour.

Sodium glutamate, which has a taste very like meat extract, is used in the preparation of certain soups and gravy flavourings, and can be used in water as a substitute for beef tea. It can be made by dissolving gluten in an acid, preferably hydrochloric acid, at a temperature below the coagulation point of the protein, adding a small quantity of finely granulated tin, and then heating the mixture under pressure with steam. The tin accelerates the hydrolysis and removes any arsenic in the acid. The solution is filtered, concentrated, and the glutamic acid hydrochloride is allowed to crystallise. The crude hydrochloride is neutralised with slight excess of caustic soda, which precipitates any tin present, the sodium and ammonium chlorides are separated by evaporation and crystallisation, and the mother-liquor is added to alcohol to precipitate the sodium glutamate.

Corn Products Refining Co.⁸ utilise maize gluten for the preparation of pure amino-acids. The protein is hydrolysed by boiling with 20 per cent. hydrochloric acid and humin substances are removed by evaporation and filtration. The pH value is then adjusted by the addition of caustic soda, and by successively adjusting the pH value to the iso-electric point of each amino-acid present these can be separately precipitated relatively pure. Care must be taken to control certain factors such as the density

of the solutions and the crystallising temperatures. Tyrosine is precipitated at pH of 2.4-3.4 followed by leucine at pH of 6-7. Two pounds of the former and 15 lb. of the latter are obtained from 100 lb. of maize gluten.

From potato-starch manufacture is obtained the exhausted pulp which, in some factories, is treated with lime to allow easier separation of the water, which is present to the extent of more than 90 per cent. After the moisture has been expelled from the pulp by means of pulp presses (see Fig. 14:1), or other mechanical means, the solid cake is used as cattle fodder. Another method, which is stated to give a more palatable fodder for cattle, is by controlled fermentation of the exhausted pulp in earthen trenches. W. Ostwald, H. Erbring and A. Siehr¹⁰ have covered the use of potato protein in soaps and detergents. The protein is removed from the factory waste waters by blowing air into the liquid when the foam so formed contains all the protein present and can be removed and the protein recovered. The use of starch, itself, in soaps is discussed on page 285.

The utilisation of rice oil for olein and stearin manufacture has been dealt with by S. Ueno.⁷

V. A. Devyatnin¹¹ suggests the preparation of pyridoxine, vitamin B complex and thiamine concentrates from the water soluble fraction of wheat embryos. From the fat-soluble fraction he proposes to prepare fats, vitamin E concentrate and sitosterol concentrate.

REFERENCES

1. W. SAGE, U.S.P. 1,187,392, 1916. (Lapsed.)
2. BURGGRAB, *Dingl. Poly. J.*, 1835, **56**, 46.
3. M. MAERCHLER, *Zeit. Landw. Central Prov. Sachsen*, 1876, 7.
4. G. DE CLAUVERY, *Dingl. Poly. J.*, 1837, **63**, 465; 1841, **80**, 399.
5. MARKL, *ibid.*, 1874, **214**, 225.
6. ANON, *Ind. Eng. Chem.*, 1937, **29**, 673.
7. SEI-ICHI UENO, *J. Soc. Chem. Ind. Japan*, 1937, **40**, 200.
8. CORN PRODUCTS REFINING CO., E.P. 528,162.
9. E. BARTOW and W. W. WALKER, *Ind. Eng. Chem.*, 1938, **30**, 300.
10. W. OSTWALD, H. ERBRING and A. SIEHR, G.P. 660,992; *Deut. Patum. Zeit.*, 1940, **26**, 185.
11. V. A. DEVYATNIN, *Pishchevaya Prom.*, 1944, No. 9, 8.

CHAPTER 15

ANTISEPTIC AGENTS AND PRESERVATIVES

THERE are two distinct conditions that may arise to worry those concerned with the manufacture and applications of starch and flour preparations, and cause spoilage of materials at some stage of the process. The first of these is bacterial action and the second is fungoid growths or mildew, and of these the second is probably the more troublesome.

Bacteria are found in starch, sometimes in large numbers, although starch is far from being an ideal or complete food for them. The bacterial count is greatly influenced by the chemical processing it has received and on the air, water and equipment with which it comes into contact. A. Frieden¹⁶ has published data showing the wide fluctuations which occur in the number of bacteria in corn starches. In general, oxidised starches have a lower bacterial count than thick-boiling starches, whilst unmodified products dried by slow methods in the presence of unlimited and untreated air contain more bacteria or spores than the same starches dried by modern methods.

Tapioca flours have a surprisingly low and uniform bacterial content. Frieden¹⁶ classifies the micro-organisms in starch into three groups, namely, (1) general, including moulds, (2) *B. coli*, (3) thermophilic bacteria. The number of bacteria tends to decrease when the starch is stored in a cool dry place, but there is an increase in bacterial activity when the starch is mixed with water prior to using it for processing. The above worker recommends the use of a combination of benzoic acid and para-formaldehyde to restrain bacteria, while he considers that copper salts are the most effective agents against moulds and yeasts (see, however, below).

It is difficult to prepare commercial starch which is free from thermophilic bacteria, a desirable feature if the product is to be used in preserved foodstuffs. One method of reducing the thermophilic bacteria population is to reduce the moisture content of the wet starch, in manufacture, to below 2 per cent., using the standard equipment, followed by heating the starch to 122° C. for 3 hours. This treatment kills all the bacteria without affecting the properties of the starch to any appreciable extent.

If 5 per cent. or more moisture is present during the heat treatment the starch may be damaged without completely eliminating the thermophilic bacteria.²⁶

Mildew is propagated or spread by the minute spores of the growth being carried by the air from place to place, and thrives on a wide variety of diets. Moisture and warmth increase its rate of growth and allow it to make full use of any favourable conditions it may find.

It cannot be emphasised too strongly that scrupulous cleanliness should be observed from the beginning of the processing to the final packing of the goods. When adhesives or sizes, etc., are to be transported the barrels should be washed out with water containing weak alkali and 1 per cent. of formaldehyde, and then thoroughly steamed with live steam. A pipe-line with side pipes can readily be fitted up in most factories so that a batch of barrels may be steamed at once, the steam being passed into the bung hole of the inverted and slightly tilted barrels. It is preferable to carry out the steaming immediately before use, so that the barrels have enough time to dry but not enough to become contaminated. If this cannot be arranged they should be stored, preferably in a dry place in an inverted position until required. Beechwood casks should be waxed after cleaning, for this assists greatly in reducing the possibility of mould spores gaining foothold.

The remarks on absolute cleanliness apply also to the condition of the vats or boilers, and apart from the danger of infection of batches, the factory in general should be kept clean in the interests of safety and efficiency of the workers.

In the preparation of sizes the temperature is generally between 95° and 100° C., and many of the spores of moulds, etc., introduced with the sizing material, or already present in the vat in the residue from previous batches, survive and remain viable, probably because the colloidal nature of the medium tends to protect them. During the sizing operations the size is passed from the vat in which it is prepared to the 'sow' or size box on the sizing machine, and losses are replaced every six or seven hours. The vat usually contains some residual size, which constitutes a good medium for mould growth, as its temperature falls below 40° C. in the interval between making two batches.

The flora remaining viable in the residue would be chiefly butyric-acid bacilli, which are capable of hydrolysing and souring the starch. Further contamination may be caused by air-borne spores. The latter also possess hydrolytic properties, and are

thus capable of rendering the medium suitable for further attack by other microflora introduced with the flour or starch itself.

In the size box on the machine the temperature at which the size is maintained during the operations would check the development of the organisms present, but these would be transferred to the cloth with the size, and when the moisture-content of the cloth had risen on storage to 8-10 per cent., the *Aspergillus* and other fungi could readily develop.³ Sometimes uncooked starch or flour is added to the size box, and this introduces another source of infection.

The fermentation of wheat flour to obtain a sizing material is mentioned elsewhere, but it may be mentioned here that when this process is carried out in the presence of an antiseptic, e.g. 8-10 per cent. zinc chloride, the process is termed 'steeping'. Bean and Scarisbrick⁴ consider this process preferable for avoiding loss of starch, but on this point there is still some controversy.

The fermenting paste is stirred from time to time in order to introduce air, which retards the growth of putrefying organisms. In the first stages of the fermentation, yeasts and bacteria increase enormously, and the sugar present is consumed with the formation of gas, but after about a week lactic-acid bacteria predominate, and most of the other organisms present are suppressed by the organic acids produced.

A sized cloth may harbour organisms derived from three sources: those applied with the size, those deposited from the air, and those already present in the cloth before processing, especially when grey goods are sized. The moulds present are chiefly of the *Aspergillus* and *Penicillium* type, and certain *Fungi Imperfecti*.

Morris⁵ has evaluated the suitability of various sizing material as nutrient media for *Aspergillus* species, taking a strong wheat flour, i.e. one with a high protein-content, arbitrarily as 100, and his results are reproduced below:—

TABLE XIII

Rice flour	108	Soluble starch	85
Cassava flour	106	Maize starch	82
Maize dextrin (acid process)	100	Sago	78
Maize dextrin (heat)	98	Farina	76
Potato dextrin (diastase) . .	97	Cassava starch	74
Potato dextrin (acid)	90	Soft-wheat-flour fermented 10	
Wheat starch	89	weeks	72

Fungi other than those used by Morris might not give the above sequence, but generally speaking starches are more resistant to the propagation of moulds than are flours. This is also generally true of adhesives made from these two types of material. Ad-

hesive pastes exposed to the atmosphere in a damp place for any appreciable time become covered with a layer of mould-growth, of which the *Aspergillus* and *Penicillium* genera preponderate. Below the layer of mould-growth is generally a region which soon shows signs of fermentation and acid-production. Pastes showing even a little mould-growth are generally rejected so as to eliminate possible contamination of other products which may be made in the factory, and also because of the unsightly appearance of a mouldy paste.

The common preserving agents used in the textile industry are zinc chloride or sulphate, barium chloride, sodium chloride, phenol, formaldehyde, cresylic acid, salicylic acid, and magnesium chloride.

Phenol and cresylic acid suffer from the drawback of possessing a very well-defined and penetrating odour, which renders them objectionable for certain uses in the textile trade, or for adhesives to be used in the packing of foodstuffs. Salicylic acid has but a slight protective action, and is expensive. It also has the defect of forming a highly coloured compound in the presence of traces of iron salts, which may contaminate the batch by solution from the apparatus or machinery used. The unsightly appearance conferred on a paste by this coloration renders it quite unfit for sale.

Aluminium chloride has been used as a mould-preventive, but it is difficult to see any advantage it possesses; when used in quantities sufficient to prevent mould-growth, it can have a very pronounced tendering action on a textile material. Magnesium chloride has been used in textile dressings for at least three purposes; to assist in solubilising the starch, to weight the material, and by virtue of its hygroscopic properties to retain moisture, so that it imparts a soft 'handle' to the 'finish'. It also possesses some anti-mildew action. Its use has to be watched, however, when it is to be applied to textiles which are to be subsequently singed as, in this case, tendering of the fibre is very liable to occur.

Formaldehyde and hexamethylene-tetramine are good preserving agents, but the latter is somewhat too expensive for general use. In a large number of adhesives and pastes, where odour is not a drawback, the addition of $\frac{1}{2}$ per cent. phenol and $\frac{1}{4}$ per cent. formaldehyde to the 'mix' is to be recommended. Formaldehyde is valuable in that it can be used in acid or alkaline pastes, and appears to form some kind of loose compound with the starch (see Vol. I) and with any protein matter present. It is therefore valuable for use in flour pastes containing a marked percentage of protein matter, i.e. those from strong flours. In

flour pastes used as adhesives its employment tends to increase the strength of a joint, because salts are, if anything, harmful to joint strength, especially if they are unduly hygroscopic, and formaldehyde is free from this drawback.

Beta-naphthol is widely used and can safely be recommended as a component of 'difficult' mixtures; it also has the advantage of having a smell less marked than that of phenol. The addition 0.25 per cent. usually suffices.

Boric acid and borax do not appear to be such good agents as one would expect, and adhesives containing them sometimes show quite a bad mould-growth, especially products made from flour or those containing some nitrogenous material, such as maize or wheat products. Generally, they have been added to the mix for quite a distinct purpose, apart from any possible antiseptic value that they may have. Dimethylglycol, encupinotoxin, furoic acid, sodium furoate, furfural, hydrofuramide, trimethylene and propylene glycols, and thymol are also strongly protective against mould-growth, but with most of these the cost is prohibitive.

Oil of sassafras and terpeneol are used by some firms, and here again several functions are combined. They are generally used where it is necessary to mask the odour of any particular 'mix' such as the odour of formaldehyde and phenol which have been added purely as anti-mildew agents.

In the paper industry the principal operations in the mills, especially the drying operations, tend in the main to reduce the bacterial count and in the finished paper the starch present tends to reduce, rather than maintain, the number of micro-organisms present.¹⁶

Sodium ortho-phenyl phenate has been claimed to be a good protective agent, and E. C. Britton and L. E. Lindley¹ suggest the use of a polychlorophenol, e.g. 2-4-5 trichlorophenol, in the presence of alkali. An I.G. Farbenindustrie patent² covers the use of 1 pt. ortho-benzyl phenol in 2 pts. of glycerol diacetate, the mixture being added to the 'mix' to the extent of 0.1 per cent. to prevent either mould or bacterial growth. The last-mentioned antiseptic is claimed to be odourless, a claim that cannot be made for the other compounds listed. Morris⁷ has also examined a number of compounds which, although efficient fungicides, possess undesirable properties militating against their use commercially. In his second paper⁷ this worker concludes that the common antiseptics do not appear to be effective in the amounts usually employed. He tested 32 antiseptics with a range of common mould fungi and found that the most efficient of the new materials tested were thallium carbonate and *p*-nitro-

phenol, the use of the latter being restricted to acid media owing to the colour it gives in the presence of alkali.

Finally, mention must be made of a compound of proved worth in the textile industry marketed by Imperial Chemical Industries Ltd. under the name of Shirilan. It is a colourless, odourless, stable and very effective agent, and its use may confidently be recommended.

Table XIV shows the preservative agents in common use and the approximate amounts which are met with in commercial adhesives or dressings :—

TABLE XIV

Alum	1-100 to 200	Phenol	1-200 to 1,000
Acetic acid	1-1,000 to 10,000	Salicylic acid	1-1,000
β -naphthol	1-250 to 1,000	Shirilan	1-1,500
Boric acid	1-200	Sodium phenate	1-200 to 1,000
Cresol	1-1,000	Sodium salicylate	1-1,000
Formaldehyde	1-400 to 20,000	Zinc sulphate	1-250
Paraformaldehyde	1-400 to 20,000		

As previously mentioned, oil of sassafras and terpineol are used as masking agents for the odour of the adhesive or size or of one of the constituents. The addition of lemon-grass oil is sometimes made with the same object, and that of oil of cloves and oil of cinnamon imparts a freshness or a 'clean' smell, which may have some psychological effect, as these oils are often included in the formula for wallpaper adhesives.

To prevent butyric, acetic and lactic fermentations in starch solutions the use of soluble fluorides has been advocated,¹⁷⁻²² an acid medium giving the maximum effect.²¹ Effront considers that hydrofluoric acid and soluble fluorides do not affect amylase and that the apparently favourable effect exerted by fluorides on the action of this substance is due to the restraining action they exert on butyric and lactic ferments. The author and other workers, however, find that sodium fluoride does affect the activity of certain amylases (see Vol. I). H. Cluss and H. Feber²² consider aluminium chloride the most effective in this respect.

It may be of interest to mention here that Barton-Wright and Tomkins²⁴ conclude that the critical moisture-content of flour for fungoid growth is 16 per cent., and they recommend a figure of 15 per cent. as being safe and that it should not be stored in an atmosphere having a relative humidity of 80 per cent. R.H. It may be noted that 14 per cent. moisture is the maximum content allowed by the Ministry of Food for Security Stock.

To sum up, the requirements to obtain a product which will keep well are : scrupulous cleanliness in every stage of manufacture and packing of the preparations ; the use of zinc salts, formalde-

hyde, phenol, or preferably β -naphthol ; or where the profits can stand the expense, the use of some of the more modern synthetic agents, such as Shirlan, which are now well established on the market.

Starch Indicator Solutions.—For the preservation of starch solution, to be used as an indicator in various titrations, mercuric iodide,^{8, 12, 23, 25} oil of cassia,⁹ 1 per cent. benzene,¹⁰ 2 per cent. benzoic acid,¹¹ traces of sodium hydroxide,¹³ metallic mercury in the reagent bottle¹⁴ and carbon disulphide¹⁵ have all been suggested. For iodometric titrations 0.5 c.c. of 2 N HCl per 50 c.c. of starch solution is recommended by N. Kano,¹⁵ but the author considers the addition of a little thymol to be the most effective and it has no effect on the titration.

Something may be said here of starch solutions used in dissolved oxygen determinations. A number of such solutions for use in iodometric titrations have been suggested,²⁷⁻³² but the majority of these require exact and elaborate preparation. A number of such solutions have been criticised because on ageing they cease to give sharp end-points as only a reddish or violet coloration with iodine is given.³³ W. S. Platner³⁴ takes advantage of the property of caustic alkali to disperse starch without affecting the starch itself.^{13, 35-38} Two grammes of starch in 300 to 400 ml. of water are prepared, 30 ml. of 20 per cent. potassium hydroxide solution added and the syrupy solution allowed to stand for 1 hour then neutralised with concentrated hydrochloric acid¹⁵ using litmus paper as indicator. If acidity does not interfere with the proposed titration 1.0 ml. of acetic acid is added as a preservative. W. S. Platner claims this indicator solution to be stable for 12 months, to give the blue colour at full intensity over this period and to be free from mould growth. H. A. Conner and R. W. Bovik³⁹ overcome the question of preserving starch indicator solutions by preparing a solubilised starch powder which is added, near the end point, to the solution being titrated. The powder is prepared by ball-milling the starch in alcohol until disintegrated, drying and regrinding.

REFERENCES

1. E. C. BRITTON and L. E. LINDLEY, U.S.P. 1,946,957.
2. I.G. FARBENIND., E.P. 396,737, 1932.
3. D. ARMSTEAD and S. C. HARLAND, *J. Text Inst.*, 1923, **14**, T275.
4. P. BEAN and F. SCARISBRICK, 'The Chemistry and Practice of Sizing,' Hutton, Hartley & Co., Manchester, 1921.
5. L. E. MORRIS, *J. Text. Inst.*, 1926, **17**, T1 and T23 ; 1927, **18**, T99.
6. BRIT. COTTON IND. RES. ASS., R. G. FARGHER, L. D. GALLOWAY, and M. E. PROBERT, E.P. 323,579.

7. L. E. MORRIS, *J. Text. Inst.*, 1927, **18**, T99.
8. M. MUTNIANSKI, *Zeit. anal. Chem.*, 1897, **36**, 220.
9. F. MOERK, *Amer. J. Pharm.*, 1904, **76**, 476.
10. F. N. ALCOCK, *Pharm. J.*, 1907, **79**, 121.
11. D. HELD, *Archiv. f. Hyg.*, 1915, **84**, 289.
12. ANON, *Chemical Abstracts*, 1917, **11**, 2648.
13. POLLITZ, *Zeit. angew. Chem.*, 1917, **30**, I, 132.
14. A. JUNK, *Chem.-Ztg.*, 1919, **43**, 258.
15. N. KANO, *J. Chem. Soc. Japan*, 1921, **42**, No. 11.
16. A. FRIEDEN, *Paper Trade J.*, 1940, **110**, TAPPI, 233.
17. SOC. GEN. MALTOSE BRUXELLES, *Zeit. Spiritusind.*, 1889, **12**, 291.
18. J. EFFRONT, *Bull. soc. chim. Paris*, 1890, series 3, **4**, 337, 627.
19. — *ibid.*, 1891, série 3, **5**, semestre 1, 149, 734.
20. — *Bull. Soc. d'encouragement pour l'industrie nat.*, 1891, **90**, 642.
21. — *Moniteur scientifique du doctor Quesneville*, 1892, **39**, 81; via *J. Soc. chem. Ind.*, 1892, v. **11**, 931.
22. H. CLUSS and H. FEBER, *Zeit. Spiritusind.*, 1898, **21**, 2.
23. R. C. TERRY, *Chem. and Ind.*, 1941, 155.
24. BARTON-WRIGHT and TOMKINS, *Cereal Chem.*, 1940, **17**, 332.
25. G. ROWE *et al*, *Ind. Eng. Chem. Anal.*, 1944, **16**, 371.
26. A. BULFER, *Rev. brasil. quim.* (São Paulo), 1944, **17**, 272.
27. C. L. ALSBERG and E. P. GRIFFING, *J. Amer. Chem. Soc.*, 1931, **53**, 1401.
28. G. FRERICH, *Apoth. Ztg.*, 1928, **43**, 599.
29. A. H. LOWE, 'Technical Methods of Ore Analysis,' 8th ed., p. 86, N.Y. John Wiley & Sons, 1919.
30. M. S. NICHOLS, *Ind. Eng. Chem. Anal.*, 1929, **1**, 215.
31. C. S. SHAPIRO, *J. Lab. Clin. Med.*, 1934, **20**, 195.
32. J. B. TERMANSEN, *Arch. Pharm. Chem.*, 1934, **41**, 533.
33. AMER. PUBLIC HEALTH ASSOC., 'Standard Methods for Examination of Water and Sewage,' 8th ed., p. 231, 1936.
34. W. S. PLATNER, *Ind. Eng. Chem. Anal.*, 1944, **16**, 369.
35. H. E. BROOKS, *Chem. Analyst*, 1918, **27**, 9.
36. G. B. JAMBUSERWALA, *J. Text. Inst.*, 1941, **32**, T201.
37. A. REYCHLER, *Bull. soc. chim. belg.*, 1920, **29**, 118.
38. N. SPASSKII, *Chem. Zentr.*, 1938, **1**, 3294.
39. H. A. CONNER and R. W. BOVIK, *Ind. Eng. Chem. Anal.*, 1944, **16**, 772.

ADDITIONAL REFERENCES

- M. VAN HAUWAERT, *Natureset. Tijdschr.*, 1936, **18**, 187. (Iodoform greatly retards diastatic hydrolysis, benzenoid hydrocarbons do not.)
- J. DARTOIS, *T.I.B.A.*, 1939, **17**, 25. (Fungicides for textile industry.)
- J. BRUYNE, *Bull. Ass. anc. El. Inst. sup. Ferm.*, 1938, **39**, 203. (Disinfectants for use in fermentation industries compared.)
- H. STADLINGER, *Kunstdüng. Leim.*, 1932, **29**, 138; *Chem. Zentr.*, 1932, ii, 160. (Preservatives for adhesives discussed.)
- CORN PROD. REF. CO., E.P. 533,023, 22/8/1938. (Free chlorine used to destroy thermophilic bacteria.)
- F. M. CLARK and F. W. TANNER, *Food Manuf.*, 1940, **15**, 39. (Thermophilic organisms in starch and sugar.)
- A. J. BULFER, U.S.P. 2,401,813, 11/6/1946. (Starch rendered thermophilic-bacteria-free by drying to 1-2 per moisture content at 130-140° F. then roasting 1-3 hours at 240-260° F.)
- S. OHASHI and H. NAKABAYASHI, *J. Agr. Chem. Soc.*, Japan, 1949, **23**, 107. (English summary. Examine 9 antiseptics for use in textile printing pastes and textile finishes based on starch, 2-4-6 trichlorophenol the best.)

PART III

THE EXAMINATION AND ANALYSIS OF STARCH AND STARCH PRODUCTS

CHAPTER 16

GENERAL EXAMINATION OF STARCH

ACCURATE analysis of commercial grades of starches may be needed in the food, textile, or adhesive industries ; detection and determination of starch in various finished products may also be required. In practice, the examination of a commercial starch consists in determining the contents of moisture, protein, mineral matter, fibre, and fat, and calculating the amount of starch present by difference. This method is not adaptable to agronomical, horticultural, or botanical problems, which require the direct determination of the starch itself. Many methods are available, but their very number is evidence that each is of limited application, either because of insufficient accuracy or because of the difficulties encountered with various materials. The determination of starch often constitutes a separate problem with each type of material encountered, e.g. the extraneous matter in different plants may vary widely in nature and amount. The starch in such cases may be accompanied by cellulosic compounds, gums, pentosans, glucosides, or hydrolytic products of starch, all of which may give rise to products which will affect the result of analysis.

The starch manufacturer and the buyer whose raw material is starch includes everything that occurs in the starch granule as 'starch,' and is interested in the amount and physical condition of the 'starch' in the product. On the other hand, botanical and other workers consider starch to be that portion which has certain physical characteristics and yields glucose on hydrolysis. From this point of view, the theoretical yield of glucose may be calculated from the various formulæ for starch. The larger the number of glucose units in the molecular chain of starch, the nearer does the factor for converting glucose to starch approach 0.9. The work of Haworth,² Richardson, and Freudenberg¹ indicates that the chain is long, so that this factor is probably close to the truth,

Some starches, e.g. cassava starch, are often not sold on chemical analysis, but according to sample and although various terms such as Superfine, Fine, Medium and Common are in use to describe various grades there is no precise specification for any of them and the terms are used in a somewhat elastic manner to describe those qualities which can be generally recognised by simple tests or inspection.

Commercial starch or dextrin should be examined for appearance (including microscopical examination for the detection of adulteration), moisture, mineral matter, protein, fat, and starch. In dextrins the degree of conversion, which is judged by solubility, stability, and iodine reaction, is determined along with the sugar-content.

Consumers often buy a sample and take a few bags of a given batch of starch to try the material for their own particular purpose such as dextrin-making, adhesives, textiles, etc. Some buyers carry out a limited number of laboratory tests adapted to give some information as to the suitability of a particular starch for the buyer's specific requirements. Thus a dextrin-maker will probably include a dextrinisation test, adhesive-paste makers a gelling power and stability test. Dextrin- and adhesive-makers, in general, prefer tapioca starch to have a low acidity although no uniform interpretation of this demand emerges from the trade (see Acidity, p. 340).

There appears to be but little evidence as yet as to whether starches from different varieties have identical properties. Kavcic,⁶³ working with potato starch, has shown that some of the physico-chemical properties from four varieties were substantially the same. He determined phosphorus-content, ash-content, viscosities, iodine adsorption, gelatinisation temperatures, etc. Winton and Winton,⁶⁴ find that the starch-content of potatoes depended considerably on local environment, and S. Woodruff (see Vol. I) has shown the influence of environment during growth on the properties of maize starch. The biochemical and anatomical properties of starch from different varieties of potatoes have been described by I. A. Veselovskii.⁶⁵

Appearance.—Starches should have a good white colour, be lustrous, and, if required for some of the finer technical uses, free from specks or dirt, but inferior grades from this point of view are acceptable for some kinds of work. This also applies to dextrins, but the colour in this case will depend on the extent of conversion, the acid used, and the starch employed.

Dextrins made from maize or wheat starch are matt, whereas potato dextrins often appear lustrous except in the well-converted

type of product. For starch and dextrins needed in first-class work, the absence of specks may be a criterion of cleanliness. A sheet of glass with a 10 cm. square marked on it is laid flat on the top of a layer of starch or dextrin spread out on paper, and the number of specks enclosed in the square determined. For potato starch the best prima grade should not contain more than 30 visible specks, medium prima 27-170, inferior prima 145-450, and starches not classed as prima 700-800.

Prima starch should be pure white, but for some purposes a faint tinge of blue or yellow is not a defect. It should not have a musty, sour, or putrid smell. The lustre of the highest grades is due to the large size of the particles, or sometimes to processing with hypochlorous acid.

'Squeak.'—Some starches such as arrowroot and tapioca squeak or creak when a heap of the material is pressed with a spatula. In the case of cassava starch this test has been correlated⁷⁵ with the results of chemical analyses and found to be a reliable indication of purity. Well washed and finely divided samples emit a distinct squeak whereas less clean and lumpy starch does not. The test is of more significance than may at first be apparent for a well-washed starch is a pure starch and when dried is readily reduced to a pure powder. Imperfectly washed starch is impure, containing protein, fibre and other non-starchy matter and is not so readily pulverised as the pure starch. Unpublished results of the author strongly support the view that with arrowroot starch, also, the squeak is a very good guide to the purity of the starch. Bad samples of arrowroot starch, however, appear to be uncommon in commerce, probably because of the greater ease of manufacture and purification of this starch. This statement refers, of course, to genuine arrowroot samples and not those deliberately adulterated with other starches or materials.

Microscopical Examination.—*General considerations.* Although starch from various plants have somewhat similar analytical figures when pure, the form of the small granules varies from starch to starch and a microscopical examination is a valuable diagnostic method in any laboratory dealing with starch products for the identification of starches. Apart from the characteristic shapes exhibited, the temperatures at which the granules of the various starches commence to swell in water is significant and readily followed with a hot-stage.

In observing this gelatinisation slightly oblique illumination is advantageous but should not be used when making measurements owing to the shadow effect on one side of the granule, tending to lead to false readings on the eyepiece micrometer. Lippman's

table of gelatinisation temperatures in degrees C. of the commoner starches, published by Hanausek is reproduced below.

	TABLE		XV
Variety.	Swelling commences.	Gelatinisation commences.	Gelatinisation complete.
Rye 45·0	50·0	55·0
Horse-chestnut 52·5	56·2	58·7
Rice 53·7	58·7	61·2
Barley 37·5	57·5	62·5
Potato 46·2	58·7	62·5
Maize 50·0	55·0	62·5
Wheat 50·0	65·0	67·5
Tapioca —	62·5	68·7
Arrowroot			
(<i>M. arundinacea</i>) 66·2	66·2	70·0
Sago (<i>S. rumphii</i>) —	66·2	70·0
Buckwheat 55·0	68·7	71·2
Acorn 57·5	77·5	87·5

Starches may be mounted in water, but dextrins, being soluble to varying degrees in this medium, should be mounted in a polyhydric alcohol such as glycerine. Microscopical examination of dextrins often gives a clue to the nature of the starch used. In one case the author found it of great value in clearing up a problem which would not have yielded readily to other methods: A potato dextrin which had hitherto shown good 'working properties' exhibited a strong tendency to 'spin' or 'fibre' (see p. 130), and microscopical examination disclosed the presence of about 40 per cent. of tapioca dextrin. The price of tapioca dextrin at this time was considerably higher than that of potato dextrin, so that the addition was not made with the object of adulteration, but was a mistake on the part of the manufacturer, who should have admixed only a small percentage of tapioca starch before roasting to give it the characteristic properties of this grade.

For examining untreated starches, a microscope having a $\frac{1}{6}$ -in. objective, and fitted with a micrometer eyepiece, is desirable. Polarising and analysing Nicol prisms and a selenite or 'polarised' plate for examinations in polarised light are also highly desirable. For the latter purpose, the sample is mounted in dilute glycerol or Canada balsam. The field should be well filled but not overcrowded. The size and shape of the granules should be observed, and the position of the hilum (*vide infra*) and the concentric rings round it should be noted, if they are present. The appearance of granules in polarised light also gives valuable information, the granules of some starches showing a dark cross or V, which disappears if the granule is fractured by grinding or heating in water, although on moistening a dry granule the markings become much more distinct, due to an increase in internal pressure brought

about by the swelling of the interior, but not the exterior, of the granule.¹²

When the dark cross is observed the hilum is located at the intersection but as the hilum becomes more eccentric the cross changes to the V form. Over-dry or gelatinised granules have their internal forces relieved and the refraction disappears. Re-moistening the extensively dried starch restores the refraction.

Lack of contrast is a drawback to microscopical work and the loss of refractiveness of starch on hydration reduces the contrast between the object and the field. This constitutes, perhaps, the greatest difficulty met with when trying to photograph a field under examination. Resort to staining is sometimes made, but it is not as a rule advisable, because it often leads to the formation of artifacts.

Generally, the size of the granule is expressed as the length of its longest axis in microns ($\mu = 1/1,000$ mm.), and the size of the largest and smallest granules should be noted as well as the average size of the mass of the particles.

The granules may be shaped variously according to source and may be polygonal, round, oval or elliptical.

The shape of the granules from any one plant may vary according to the environment during growth. Maize starch grains which are very angular and highly refractive result from growth in a glutinous matrix which later dehydrates and resists deformation by the growing starch granule. Starch from the crown of the maize kernel is very loosely packed and presents the round outline of granules which are not constrained by their encompassing tissues during growth. Such granules are the fragile type, readily injured in grinding operations. Potato, arrowroot and tapioca starches are others formed in conditions free from physical constraint and under higher moisture conditions. These, also, are rounded, elliptical or non-angular in outline and readily injured in grinding. Millet and rice starches are others which grow under restraining conditions and these, again, are tough and highly angular. The polygonal form shown by such granules as the latter probably results from the close packing of the granules during growth. Such granules may not be completely separated during milling and are sometimes referred to, erroneously, as 'compound granules,' true examples of which are extremely rare.

A spot can be seen on granules of some starches and is called the hilum. It is thought to be the nucleus around which the granule has grown.

The position of the hilum varies in size, shape, and position

for various starches, and so aids identification when examining mixtures. When dried to a low moisture-content, the hilum often appears as a star-shaped crack, the type of crack varying with the type of starch. The striations, if present in a granule, are made more pronounced if the starch is treated with dilute chromic acid solution and examined with oblique illumination.

It should be stressed that known samples of the various starches being examined or sought for should be available for comparison since no truly ideal mountant for starch for permanent slides has yet been evolved and comparison with drawings and photographs has not the same value as the comparison with actual, genuine starch specimens. As mentioned above water can be used for mounting starch granules. Canada balsam has rather too high a refractive index to be really suitable, although it is satisfactory for polarised light examination. The preparation of semi-permanent slides can be made using Euparal as a mountant, the starches keeping well and undergoing no structural or dimensional changes in this mountant. Armitage recommends dioxane-sandarac gum as a useful mountant.

According to E. Berliner⁵² clove oil is a valuable mounting medium as it makes the fissures in diastatically corroded starch granules very prominent.

In examining mixtures of starches, two methods are generally employed: (1) differential staining of the components; or (2) differential swelling in various reagents.

Staining Methods.—Starches appear to vary in their affinity for organic dyestuffs which allows the detection of granules of one starch in the presence of others to be carried out more expeditiously than a straight examination in the normal manner. F. D. Armitage⁷⁷ has pointed out that the dyestuffs used in this work may be variable in their staining reactions. It is therefore desirable to test samples of the same dyestuff from different sources with known starches until a sample of dye giving the desired reaction is found. This applies particularly to the Soluble Blue, Orcein and Safranin mixture used in Unna's method *vide infra*. Armitage⁷⁷ points out that Anilin Blue WS (C.I. No. 707) which has a slightly different formula from Soluble Blue, is the only one giving the positive reaction with the Unna technique.

Dyestuffs are not homogeneous products and research still awaits those interested as to which component of a dyestuff, it may be an impurity, causes the actual coloration of a starch, and the optimum conditions of staining. Little, if anything, is known of these matters at present and an investigation into the mechan-

ism of staining of starch with dyestuffs would be illuminating in several directions.

To stain specimens to be permanently mounted Armitage proposes the following solutions :—

1. Aqueous Methylene Blue solution. 2. Safranine O. 3. Methyl Violet. 4. Picric Acid solution, followed by washing in alcohol and staining with the Methyl Violet. 5. Chlorazol Fast Red K. 6. Congo Red. The latter in water is a temporary mountant giving a red background whilst the granules are unstained unless they are damaged (see p. 322).

Whereas Metachrom Red G. Agfa does not colour cereal starches,³ it stains potato starch a bright golden yellow. The sample of starch to be examined in this way must be exactly neutral to litmus in reaction because, in the presence of acid, wheat starch is also stained. E. Unna⁴ proposes a test, based on differential staining, to distinguish between potato, rye, and wheat starches. The suspected mixture is suspended in a 3 per cent. phenol solution for 24 hours and then a drop is transferred to a slide and allowed to dry. The slide is immersed in a solution of a mixture of Soluble Blue, Orcein (a carmine-red crystalline powder obtained from lichens, species *Roccella* or *Lecanora*), and Eosin in aqueous alcohol for 10 minutes, and after washing is immersed for 15 minutes in a solution of Safranine. It is then removed, washed, and immersed in a 0.5 per cent. solution of potassium dichromate for 30 minutes and again washed, first with water, next with alcohol, and then with xylene; finally it is mounted in Canada balsam. In this manner the potato starch is stained dark red; wheat starch, pink; rye starch, yellow to brown; and the gluten, blue. Potato starch is also detected by its characteristic behaviour when treated with Löffler's solution of Methylene Blue and examined under polarised light.⁵

A. P. Schulz and G. S. Steinhoff⁶ suggest a mixture of Methyl Orange, Fuchsin and Methyl Green for the identification of potato starch which is stained blue. Neutral Red colours this starch pink. They consider that Metachromate G. or Congo Red (C.I. No. 370) is the most satisfactory if the starch is in a paste form or if the grains are corroded. No sharply distinguishing colour test for starches other than potato starch is available, but they can generally be identified by the above dyestuffs augmented by Safranine and Thionine. To detect potato starch in bread G. Schutz and L. Wein²⁴ use Thionine, which stains potato starch lilac, the rest of the potato substance reddish-violet or blue, but is without effect on wheat or rye. W. Neuwohner⁵⁷ and Klauss⁵⁸

both use iodine/potassium iodide solution for the detection of potato meal in wheat meal as the granules of potato starch stain with a greater intensity of colour than wheat starch granules. The examination of wheat starch by staining methods is more fully dealt with on p. 322.

When using potassium iodide-iodine solution for staining starches it is desirable to not exceed a strength of 0.3 per cent. otherwise the granules stain so deeply that the surface characteristics are lost.

Swelling Methods.—W. H. Symons⁷ suggested stirring the starch with alkalis at various concentrations and noting the number of grains swollen at each concentration as a means of distinguishing between the various starches. He measured the concentration of sodium hydroxide solution required to gelatinise the majority of granules and found concentrations between 0.5 and 1.5 per cent. to be most suitable: 0.1 gm. starch was stirred with 1 ml. of the caustic soda solution and examined under the microscope. The following percentage concentrations are those which just swell the majority of the granules of the starches named: potato, 0.7; oat, 0.8; tous les mois, wheat, and sago, 0.9; maize, rice, and cassava, 1.0. Later, K. Baumann⁸ used the fact that maize starch is less readily swollen by 1.8 per cent. potassium hydroxide solution than wheat or rye starches, and that the latter are ruptured more readily than the wheat starch. After the gelatinisation has taken place the maize starch can be made more apparent by staining with iodine.⁹ Rye starch^{10, 81} is also differentiated from other starches in that the granules gelatinise faster when suspended in a 9 per cent. solution of sodium salicylate. At the end of an hour the larger granules have swollen and show no cross with polarised light. J. A. Radley has found that 38 per cent. formaldehyde solution swells potato, tapioca, wheat and maize starches in that order, the swelling of the first two being very much more rapid than is the case with the last two.

Identification of the starch by microscopical examination is readily carried out and, owing to the characteristic shape of the granules, adulteration is readily detected. Adulteration of one starch with another is sometimes made more difficult owing to similarities between the two starches; wheat starch adulterated with small quantities of rice starch is a case in point.

Destruction of the structure of the starch, e.g. by any of the methods already described, practically eliminates the use of the microscope as a means of investigation. Fortunately, Giri and Bhargava¹¹ have found a method of narrowing down the

possibilities of a sample being a member of a particular group. The method depends on the formation of characteristically coloured zones when starches are impregnated into an agar medium, hydrolysed with amylase, and then flooded with iodine solution: 0.8 gm. of the sample to be examined is added to 100 ml. of boiling water and, after boiling 1 minute, the liquid is filtered through muslin and then added to an equal volume of a 1 per cent. agar medium, which has been adjusted to pH 4.6 by the addition of 0.2 N acetate buffer. If salivary amylase, malt amylase, or takadiastase is to be used, the pH value is adjusted, before mixing, to 6.8 by means of N/15 phosphate buffer. The solution is then plated out into petri dishes, one drop of the amylase solution dropped into the centre of the plate and allowed to diffuse for 24 hours at room-temperature. The concentration of the amylase should be 1 in 5 for saliva and 0.1 per cent. in the case of takadiastase.

After 24 hours the surface of the solution is flooded with N/200 iodine solution, and a few minutes later the coloured zones may be examined. Various cereal starches and flour have characteristic zones, and the use of different amylase preparations gives a still further differentiation, as the diffusion zones developed by each type vary in width and intensity of colour with the source of the amylase. Wheat starch with salivary amylase gives a central colourless zone surrounded by a deep blue zone. Malt amylase, however, gives a central zone of deep green surrounded by a diffused violet zone, whereas takadiastase produces a central blue zone surrounded by an edging of violet. Maize, jowar, and bajri behave in a similar manner. Rice, ragi, and barley, however, give with malt amylase a deep blue instead of a green central zone.

A similar method for the examination of dextrans that have been treated with water would be of great value.

Some work,¹³ however, has been carried out on the identification of swollen starches where the disorganisation of the structure is not too great to allow certain conclusions to be drawn as to the nature of the starch present in the paste. This work is discussed below and on p. 348 the potentiometric measurement of iodine absorption is described. This latter technique holds possibilities of characterising mixtures of unknown, pasted starches.

Potato Starch.—The granules of this starch vary greatly in size; the largest are often egg-shaped, and the majority are flattened ellipsoids, but the smallest may be perfectly spherical. The granules generally occur singly, although compound granules containing two or three units are seen on rare occasions. The

size varies from 15μ to 100μ , but O. Hoyer,⁵⁶ who has examined samples from many sources, considers the upper limit to be 121μ , and in the trade the starch with the highest average granule size is considered the best grade for some purposes.

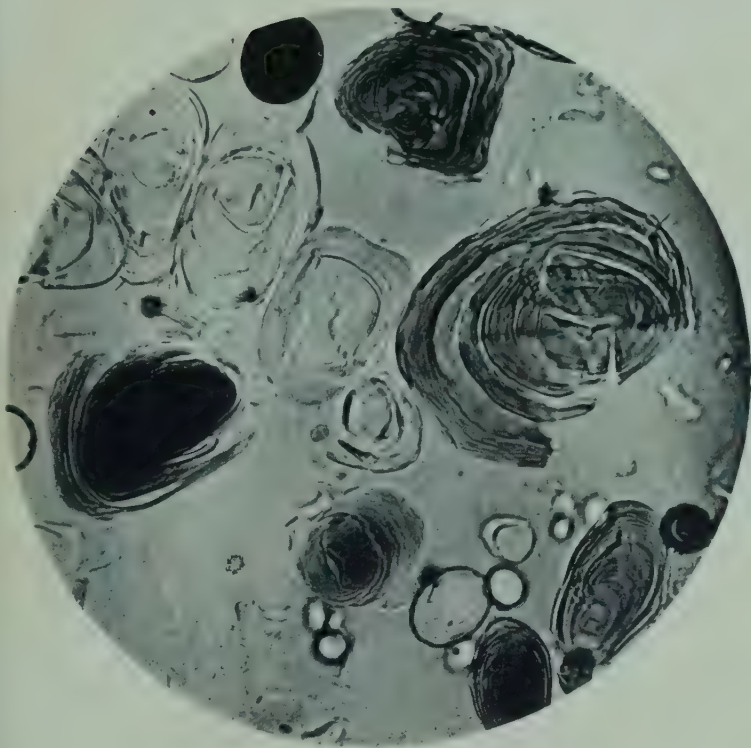
O. Saare has measured the average length and breadth of granules of various grades of potato starch and has found the following values: best quality 35.5μ , superior prima 32.8μ , second product prima 21μ , secunda 16.9μ , tertia 12.5μ .

The cross seen with polarised light is well defined but irregular in shape, and is centred in the hilum, which may be seen as a well-marked black dot or sometimes as a small split, and eccentrically situated near the smaller end of the granule. On rotating the analyser through an angle of 90° , so that the 'field' is light, the grains appear dark and the cross appears light. The cross appears in all grains, the very smallest showing it quite distinctly.

When gelatinised the granule opens up partially along the median line, the parts of the granule on both sides of the opening elongating as gelatinisation proceeds to give as a final result a ring of more or less irregular shape which shows no cross in polarised light. Badenhuizen⁷³ considers the swelling to take place exclusively tangentially, the layers confluent until finally they form the outer sac. He considers that the swelling is not due to internal pressure, but to the peripheral layers pulling asunder the internal ones. One result of this is the formation of the apparently free space often seen in the centre of granules soon after swelling has commenced. R. W. Kerr⁷⁴ does not agree with Badenhuizen's explanation but considers that the organisation of the granule is both radial and concentric and for O. A. Sjostrom¹³ has noted that the hydration develops peculiar units of rounded form, arranged in rather an irregular manner, and often showing individual striations which are usually obliterated with increased swelling at higher temperatures.

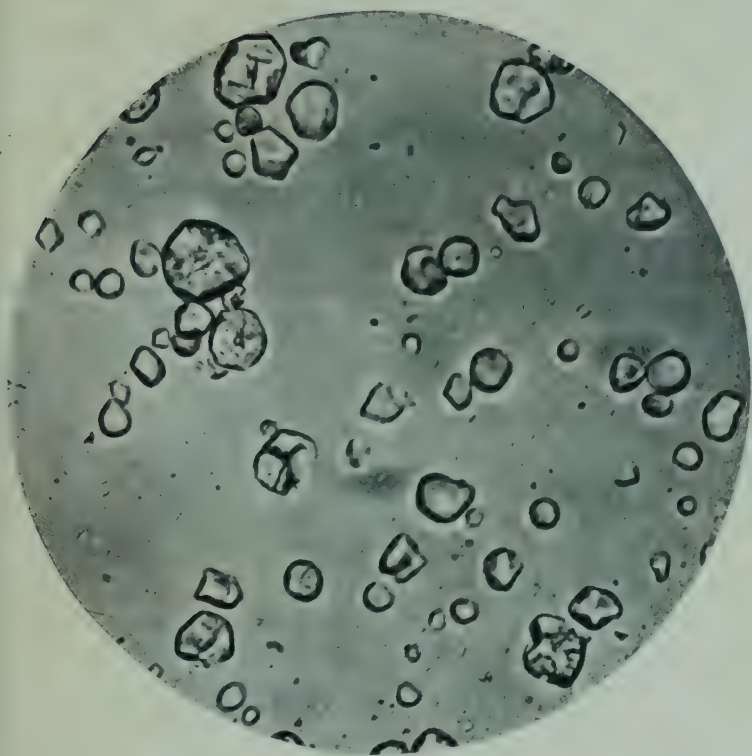
The granules of thin-boiling starches made from potato starch tend to swell more in relation to the original size than do those made from tapioca or maize starches. The phenomenon shown by the unmodified granules can still be observed in the thin-boiling type. With potato dextrin mounted in water and glycerol the peeling off of layers can be observed (see Photomicrograph No. 1), and the difference between the mode of disintegration of potato dextrin and thin-boiling potato starch is greater than with cereal starches.

With sweet potato starch and also with canna starch when the elastic limit of the swollen sac is reached the granules virtually explode. Hydration and swelling of a granule may be localised



Photomicrograph No. 1.

No. 1. Yellow potato dextrin swelling in aqueous glycerine. Note the method of dissolution (see Vol. I, p. 60 and Vol. II, p. 320).
 No. 2. Thin-boiling maize starch made by oxidation. Granules easily crushed. [Facing p. 320.]



Photomicrograph No. 2.

in certain spots and retarded in others. The swelling may therefore not be uniform in respect to the concentric layers. Such behaviour is, however, only seen at the outset of gelatinisation and not in the final stages.

According to V. Vilikovski⁵⁵ very dry seasons diminish the size of the granules formed in the potatoes, and to obtain large granules potash fertilisers should be used.

Wheat Starch.—Wheat granules are thin and lenticular in form; perfectly circular grains are much more rare than in rye starch, and do not show any distinct striations. The hilum is only observed in a small number of grains, and appears as a dot situated eccentrically or occasionally as a cleft hilum. Different varieties of wheat yield starch in which the limits of size of granules vary to a marked extent. The large granules may vary from 25μ to 35μ with a centric hilum, whereas the smallest granules are from 2μ to 8μ , and show no hilum. The upper limit for size is, according to O. Hoyer,⁵⁶ 55μ .

When heated in water the granules swell, and near the boiling-point they assume a peculiar and characteristic curved shape, which has been used by Sjostrom¹³ to identify wheat starch in several technical products where identification by other means would have been impossible. Rye starch shows a similar behaviour.

Brucknor and Thomas²⁵ detect maize starch in wheat flour by observing under the microscope the action of 0.16 N potassium hydroxide on the flour, the maize starch being unaffected. They have also elaborated a biuret test to distinguish between the two starches. E. Vogt⁴³ uses a stain of Congo Red in indian ink to detect adulterants of wheat flour, whilst T. E. Wallis⁴⁴ detects wheat in barley starch by noting if any granules have a diameter greater than 40μ , as some wheat starch granules exceed this size. N. I. Ozolin⁴⁹ gives a colorimetric method for detecting corn flour in admixture with wheat flour, whilst the detection of rye flour in the latter is dealt with by C. Schweizer.⁵⁰ The turbidity produced when an aqueous extract of flour is treated with ferric chloride and kept for 2 min. in a water-bath is used by H. Kühl⁵¹ to detect rye in wheat flour. J. König and F. Bartschat⁶⁸ have dealt with the estimation of rye in wheat flour, and R. Strohecker⁶⁹ has described the identification of these two flours by means of their aqueous extracts.

Wheat Flour.—It is very important with certain wheats that mechanical damage to the starch be detected. The type of damage which is found associated with an increase in maltose figure (see p. 192), due to one form of rolling as opposed

to another, is not obvious, but such damage is nevertheless highly characteristic.

Damaged granules do not appear cracked but have a curious flat appearance and a thin faint outline. Owing to their attenuated appearance C. R. Jones⁶⁶ has termed them 'ghosts,' and they are more easily detected in flour by suitable differential staining. Aqueous Congo Red solution (0.1-0.35 per cent.) does not stain sound starch, whilst the 'ghosts' are all stained uniformly an orange-pink, the gluten is coloured a bright brown. Care is sometimes required (especially with low-grade flours) to avoid confusion arising from the presence of endosperm cell-wall tissues which stain a vivid pink. With large particles the outer margin of the gluten is heavily stained but the interior escapes.

Staining by irrigation is not to be preferred, as it can lead to uneven distribution of the stain over the field and tends to derangement of the field under observation. It is thus preferable to make up the preparation from the start with the stain solution. A few important features of this staining are that it is uniform, the starch granules either staining alike or not at all. Every stained granule is uniformly stained and has the same tint. Very occasionally a granule is seen which is sound on one side but swollen to a 'ghost' on the other, rather like an oyster shell. One side has the 'solid,' strong outline of sound starch, whilst the other has the usual faint enlarged 'ghost-like' outline. In such a case the 'ghost' portion stains uniformly and the other remains unstained. Except in these rare cases the 'ghosts' are uniformly stained around the circumference. The zone of stained material in any one 'ghost' increases in width uniformly from the circumference inwards as the colour is taken up evenly until, at last, the unstained point at the centre disappears, leaving the 'ghost' uniformly tinted. Congo Red stains thus very rapidly and is not easily followed. It is slower and more easily followed if dilute iodine solution is used. An iodine/potassium iodide solution of more than a certain concentration stains starch, sound and damaged alike, a deep purplish-blue. If 0.02-0.03 per cent. iodine in 0.07 per cent. potassium iodide is used the 'ghosts' stain intensely blue but the sound granules never stain more than a faint purple. The staining process is reversible and the colour, due either to iodine or Congo Red, can be removed by irrigation with pure water, the colour disappearing from the circumference first and the centre last. This process of staining and removal can be repeated many times on the same granules, but after several repetitions the intensity of staining of the 'ghosts' falls.

The microscopic appearance of the 'ghosts' suggests that they are formed by a peripheral cleavage between upper and lower dish-shaped skins of the initially sound lenticular granules. Once the peripheral cleavage is brought about the stain enters uniformly from all peripheral points and colours the inner starch but not the skin. The repeated staining and irrigation leading to a weakening of the intensity of coloration suggests that the inner starch slowly dissolves away.

Another form of damage which may be observed in starch granules is shown by the presence of fissures in the granules. It should be pointed out that the 'ghost' form is specifically the result of flour-milling processes generally. The cracked granules behave as sound granules when treated with the above stains, but C. R. Jones⁶⁶ considers that on long standing in contact with the stain they do eventually take up the stain and become uniformly coloured.

On germination of the grain, fissures, or 'pits', as they are called, appear in the granules, but even when this 'pitting' has reached an advanced stage the granules do not stain with Congo Red. This suggests that in ordinary damage of wheat starch it cannot be a question of removal of an outer resistant envelope as has been suggested by Pulkki. The weak iodine solution, mentioned above, will stain them to a deep purplish colour, not the pure blue shown by the 'ghosts'. Granules heated in water to just above the gelatinisation point appear, stain and behave similarly to 'ghosts'. Making up a suspension of flour containing 'ghosts' with a highly diastatic malt extract solution containing Congo Red the 'ghosts' practically disappear in ten minutes at room temperature.⁶⁶

When wheat starch is gelatinised by heating in water above 65° C. the granules swell and then appear to 'curl' so that they resemble a fat grub curled up in shape.¹³

Estimation of Oat Flour in Mixtures with Wheat Flour.—

The Research Association of British Flour Millers⁷⁸ have studied the determination of oat flour in admixture with wheat flour. They find oat endosperm contains a number of compound starch granules, not found in wheat endosperm, which may be recognised and counted under the microscope. After making up mixtures containing known amounts of oat endosperm and counting the number of compound granules in each a curve is plotted connecting composition of the mixture and the compound granule-count.

Thirty milligrams of the sample to be examined is suspended in 2 ml. of a thin gum tragacanth mucilage containing 0.05

per cent. of Congo Red and a trace of ammonia, the mucilage being first cleared by centrifuging. The protein, cell wall and damaged starch granules are stained pink while the single, wheat starch granules remain uncoloured and the compound oat granules appear grey. One drop of the mixture is placed on a haemocytometer slide and covered with a cover slip, thus ensuring a definite volume of liquid being enclosed within a marked square. The compound granules lying within this square are counted and the percentage of oat flour in the mixture found directly by reference to the composition/count curve prepared as described above. This curve, incidentally, is a straight line passing through the origin so that only a few mixtures are required to obtain data for its construction. The method has been used between the range of 3-10 per cent. of oat endosperm, and, basing each figure on the average of 8 fields, the error to be expected is about ± 0.2 per cent.—i.e. 5 per cent. may be counted as 4.8 or 5.2 per cent. A skilled worker requires about 3 hours to make an estimation on a single sample.

Whole compound oat starch granules vary in size and contain from 3 to 50 granules. Each complete grain is counted as a unit. Theoretically, the method is only sound if the compound grains of different sizes occur in similar proportions in all oats. It is, therefore, of interest to note that one calibration curve has been found to apply to 3 entirely different samples of groats. A further point is that the oat endosperm next to the bran contains relatively few large compound grains, but this fact appears to be unimportant in the present connection.

It is usual to find fragments of broken large grains, recognisable by their broken, jagged outline. Since the number of broken grains varies from sample to sample according to its method of preparation, they should not be ignored completely, but at the same time each fragment should not be counted as a unit, but weighted according to size and shape, but this assessment is a matter for the individual worker, having in mind his analysis of the control samples forming the standard curve.

Occasionally a number of large, well-formed compound granules are found which do not show the characteristic reticulate markings very clearly, especially at low magnification due, presumably, to the granules being cemented closely together; at low magnifications, these grains appear denser and darker than the ordinary wheat starch grains, sufficiently so to make them recognisable with experience. Examination under higher magnification, however, always brings up the reticulate markings clearly. Care must be taken not to push a high-power examin-

ation to the extreme limit, as a very close examination may distinguish some wheat starch with reticulate markings. These, however, are always very shadowy surface markings, possibly the result of enzyme action, whereas in the compound grains they obviously exist in depth throughout the granules.

It should be noted that the compound grains disintegrate and disappear if allowed to stand in the mucilage for many hours, e.g. overnight.

Estimation of Maize or Rice Flour in Mixtures with Wheat Flour.—It may be necessary to detect and estimate maize or rice flours in admixture with wheat flour. The microscope will establish the fact of the addition and will determine its nature. The extent of the addition can be determined either by the lycopodium method of T. E. Wallis,^{106, 107} which is based on the quantitative microscopical examination of admixtures of the sample with definite quantities of the spore of *Lycopodium clavatum* or by one of the methods based on differential swelling of starches from different plants.

M. Nyman¹⁰⁸ did not find much difference in the gelatinisation temperatures of various starches, but noted a decided difference in times required for swelling at a given temperature. Since granules of the same starch have individual gelatinisation temperatures this is what might have been expected. With chemical swelling methods a sharper distinction is obtained between the swelling of different kinds of starch. K. Baumann's method (see p. 318) uses 1·8 per cent. potassium hydroxide as the swelling agent. After 2 minutes shaking with this reagent wheat, potato and barley starch grains are ruptured, but those of maize and rice are not. When dealing with flour the alkaline solution is treated with a little hydrochloric acid (4-5 drops of 1·4 to 10 ml. of solution) shaken and examined under the microscope and care should be taken that the liquid remains alkaline otherwise protein precipitates.

M. M. Taha El-Katib¹⁰⁹ has used the method as a basis for a chemical estimation. The adulterated flour is sifted through a 90-mesh sieve, dried at 100° C. for 24 hours in an oven and about 1 gm. of the dried flour accurately weighed out and transferred to a 100 ml. graduated flask using 1·8 per cent. potassium hydroxide solution, and rinsing the weighing bottle with more of the same solution. The flask, now about half full is shaken and 3 ml. of dilute hydrochloric acid (1·4) added and the volume

made up to 100 ml. with more potash solution. The flask is then shaken at intervals for 15 minutes. Twenty-five mls. of the suspension are then measured into a dry, weighed centrifuge and centrifuged at 1,000 r.p.m. for 15 minutes, the liquid decanted and the residue suspended, in the tube, in 1-4 hydrochloric acid and again centrifuged after 5 minutes' treatment. The washing process is repeated until the acid washings fail to give the starch iodide test and then the residue is washed once with the alkali solution and then with water until no longer alkaline. After drying in the oven at 100° C. to constant weight the amount of residue is found.

The object of the sifting is to retain much of the fibre of the flour which would affect the result. The material weighed at the conclusion of the work will be maize starch or rice starch. If maize flour alone has been used for adulteration the amount added can be calculated from the weight of maize starch found.

K. Nehring and J. Schütte¹¹⁰ have examined the various methods for estimating rye and potato flours in wheat flours and prefer the microscopical examination and count method.

Rye Starch.—Excepting that they are larger and thicker, the granules of this starch appear similar to those of wheat, the majority being spheroidal in shape, and among the numerous smaller granules bell-shaped ones are sometimes seen. The granules show very fine striations, radial from the hilum as well as concentric, and the size may go up to 50μ , although the average diameter is of the order of 40μ , 6.5-9.0 per cent. having a diameter greater than this. J. G. A. Griffiths finds that 5-11 per cent. of the granules of diameter greater than 10μ had stellate hila.²⁶ In a few granules the hilum may be composed of three fissures instead of four.

With gelatinised, thin-boiling rye starch, indications of a micellar structure can be seen if an immersion lens is used.¹³

Rye starch gelatinised in hot water show the same characteristic 'curled' shape as that shown by wheat starch granules.

Rye flour is detected in wheat flour by the precipitation of characteristic threads from the flour extract when acetone is added, and bean flour coagulates ferric oxide sols in a similar manner to aleurone cells.⁵²

Barley Starch.—The granules of barley starch may be bulb-shaped, elliptical, or circular in outline, and in general are not so perfectly shaped as those of wheat and rye. The large granules vary in diameter from 20μ to 35μ , and the smallest granules from about 2μ to 6μ . The hilum is absent, but in the largest grains some show striæ, but the hilum is observable even less often than

in wheat starch. Barley has a large number of very small granules, whereas wheat contains comparatively few. These small granules are irregular in shape and seldom exceed 8μ . The black cross in polarised light is generally very indistinct and, in many cases, absent.

Maize Starch.—Maize-starch granules vary in size from 10μ to 25μ , although starch of modern manufacture contains a small proportion of granules of about 5μ diameter, and are usually polygonal, although many rounded granules from the interior of the endosperm are found. If the corn is of a soft and mealy variety such as Mandan Corn, the starch obtained from it contains a preponderance of rounded granules having an average diameter of 13μ – 15μ . Pickens and Englis⁷¹ find that the granules of hard corn starches such as Kutias are smaller and less rounded than those from the soft corn. The hilum is always strongly marked, and is starred with fissures, but no striæ can be observed. The polarisation crosses are distinct.

In thin-boiling maize starch made by treatment with weak acid, the structure is not greatly altered. With 50-fluidity granules the characteristics of an untreated pasted granule are largely retained, but the granule is smaller, and cracks in the outer layer are more pronounced, becoming very pronounced in a 75-fluidity starch. In a 90-fluidity starch the radial cracks are deeper and disintegration begins to take place along concentric lines of cleavage.¹³ The increase in volume of these granules is much less marked than in the other grades, and results in a lower paste viscosity. Using an oil-immersion lens of high magnification, Sjostrom¹³ was able to distinguish concentric rings of micellæ of about 0.3μ in diameter when a chlorinated starch was examined. The photograph by Radley and Young of untreated maize starch, however, shows the concentric rings quite clearly in several granules. Maize may be detected in wheat flour by its swelling in paraldehyde⁵² or by its resistance to staining by mucicarmine.

Cassava Starch.—The granules of cassava or tapioca starch are similar to maize starch in average size, but variations are encountered, depending on the origin of the starch. They are round, with a flat surface on one side that contains a conical pit extending to the excentric hilum, which is well defined; some granules are practically circular. In polarised light a well-defined cross is observed. The smallest granules range from 5μ to 15μ , whilst the largest measure from 25μ to 35μ with intermediate granules of 15μ to 25μ . Apart from the truncated shape, this starch has very few characteristic features. J. A. Radley has noted the peeling off of layers from tapioca dextrin similar to

that shown by potato dextrin. These layers are less in number than in the case of potato dextrin, and not so easily observed. They served, however, to distinguish between a dextrin and a soluble starch. A 60/40 ethylene glycol/water mixture forms a good medium for this type of work. Dry heat apparently weakens the granule structure along concentric lines,^{13, 72, 73} whereas acid treatment weakens the structure in a radial manner. Both unmodified and modified starches of many species when crushed by pressure between glass plates break up by the formation of radial fissures. The radial fragments show no tendency to swell in cold water so that imbibition and swelling are functions of the radial units. If these units in turn are disorganised by ball-milling so that both radial and concentric lines of cleavage are disturbed the starch will swell in cold water.

F. Robertson-Dodd⁶¹ found some pods of linseed grown in a wet summer contained starch granules which were indistinguishable from those of tapioca. Generally the starch-content of mature linseed is negligible, and when starch is found it is usually taken as evidence of adulteration. This worker⁶² has also called attention to the similarity of the little-known starch—that from unripe tomatoes—to immature linseed and to sweet-potato starch.

Rice Starch.—The granules of rice starch have the smallest size of the ordinary starches, the diameter varying from 3μ to 5μ . They resemble oat starch somewhat, but are uniformly smaller, and they are definitely polygonal. The centric hilum is difficult to see, and striæ are visible only after treatment with dilute chromic acid. Compound grains composed of several granules are sometimes observed, the whole having an angular outline. They do not appear to show any cross in polarised light.

M. Wagenaar⁷⁰ detects particles of rice in wheat, rye, barley, oat and buckwheat flours by staining with Fuchsin S. This acid dyestuff is absorbed by the protein granules of the rice, and the peculiar distribution of these stained granules in the rice grain gives a characteristic appearance to the particles of rice flour.

Pea Starch.—This starch has special features which are characteristic of the leguminous starches. They are translucent, rounded in outline and irregularly reniform in shape, whilst some are more or less elliptical. Both ends of the granule are similar, unlike the egg-shaped granules of some potato granules.

The granules are strictly uniform in size, and the hilum is a dark slit lying in a shallow depression running along the long axis. Unless fractured, the granules never show a stellate hilum, and where the hilum is absent the depression can still be seen.

Concentric striæ are visible, and with polarised light a dark V is seen at each end of the granule, the apex of each touching the end of the hilum. According to Berliner⁵² the cleft hilum is not preformed but occurs only in water or other starch-swelling media as a consequence of the sudden expansion of the granules.

Arrowroot Starch.—Table XVI gives the microscopical appearance of arrowroot starch which is used in the foodstuff industry. Genuine arrowroot starches, i.e. those prepared from *Maranta arundinacea* in widely separated localities appear identical under the microscope. It is found in the trade under the names of St. Vincent, Natal, West Indian, Jamaican or Bermuda Arrowroot. Their behaviour when a 1 in 40 suspension of the starch is poured into two and a half times the volume of a 2 per cent. potassium hydroxide, stirred and allowed to stand for 5-10 minutes gives a good differentiation between Bermuda, St. Vincent and Natal Arrowroot starches.⁹⁶ The first gives a clear, faintly blue liquid with no deposit; the second gives a white deposit of swollen granules; the last partly gelatinises and gradually settles to a transparent jelly with a clear supernatant liquid. It is pointed out that the differences may be due to the method of manufacture and more recent samples require examination to check if the test gives different results now, some 33 years later. Some varieties, possibly related to 'Brazilian Arrowroot' or *Manihot*, show numerous truncated granules.

Sago Starch.—The granules of this starch resemble those of arrowroot and medium-sized potato starch granules. The size varies between 15-65 μ , mostly between 20-60 μ , and the granules are oval or egg-shaped, with some truncated oval granules. The hilum is excentric and the polarisation lines cross it in irregular patterns. The striæ are faint and concentric and seen on the more fully developed, larger granules. Both sago and arrowroot starches, when gelatinised with water, appear as smooth, bag-shaped sacs which are not destroyed by boiling. The swollen sago granules nearly always show a well-defined crater-like opening at the end of the granule which allows them to be distinguished from the swollen arrowroot granules which are more irregular in outline and the openings are large with indefinite contours.

The granules of *Shoti* starch resemble those of arrowroot, being elongated in shape.⁹⁸ This starch is much more readily hydrolysed than maize or rice and contains more amylose than maize, rice or potato starches.

Table XVI shows the various characteristics of various other starches that may occasionally be met, although a number of them are of no industrial importance.

TABLE XVI
Microscopical Characteristics of Various Starches

Name.	Source.	Granule Size.	Granule shape, or 'kettledrum'.	Hilum.	Striae.	Fissures.	Comments.
1. Acorn.		5-20 μ .	Hemispherical, or 'kettledrum'.				Simple and compound granules.
2. Canna.	<i>Canna edulis</i> , <i>coccinea</i> .	10-130 μ , most frequent— 60 μ .	Elliptical, oval, oyster or reniform.	Round and ex- centric.	Distinct.		
3. Curcuma.	<i>Curcuma species</i> (East Indian arrowroot).	30-60 μ .	Oval, elliptical, al- most rectangular or rounded, thin.	Punctiform and very excentric.	Very distinct.		
4 "	<i>C. Leucomorhiza</i> .	Generally 105 μ ; up to 145 μ .	—	—	—		
5. Batata.	<i>Ipomoea batatas</i> . Brazilian arrowroot.	Components— 10-50 μ . Simple 8-25 μ .	Components—often hemispherical.	Distinct and ex- centric. Centric or sl. ex- centric.	Well marked. Distinct.		Some compound granules 2-12, but generally 4-5 components. Mostly single. Some simple.
6. Banana.	<i>Musa paradisi-</i> <i>saca</i> .	Longest diam. 7-58 μ , gener- ally 24-48 μ .	Round to rod shaped.	Distinct, very ex- centric.	Well marked.		
7. Buckwheat.	<i>Polygonum</i> <i>fagopyrum</i> .	4-15 μ chiefly 9 μ .	Simple polygonal similar to rice.				Contains characteristic compound granules of 2-9 components which are somewhat rounded.
8. Arum.	<i>Arum esculentum</i> .	3-27 μ chiefly 13-20 μ .		Well marked.	Indistinct or ab- sent.	Radial from hilum.	Compound granules 12-10 components of unequal size.
9. Broad Bean.	<i>Vicia fabia</i> .	20-40 μ .	Simple reniform, oval or rounded.	Centric.	Visible but not marked.	Occasionally, from hilum.	
10. Bullrush Millet.	<i>Pennisetum</i> <i>typhoides</i> (Nigeria).	8-25 μ .	Irregular or round, polygonal.	Centric.	Not visible.	Occasionally.	
11. Chestnut.	<i>Castanea vulgaris</i> .	1.5-30 μ . Only few of intermediate sizes	Variouly shaped. Large—three or four-sided, heart, kidney or club shaped. Small—	Not observable.	Not visible.		Occasional twin and triplet granules.

<i>Name.</i>	<i>Source.</i>	<i>Granule Size.</i>	<i>Granule Shape.</i>	<i>Hilum.</i>	<i>Striae.</i>	<i>Figures.</i>	<i>Comments.</i>
12. Fritillaria.		Mussel and bean shaped granules. 32-71 μ . Breadth 27-55 μ . Spherical 9-17 μ .	Various. Mussel shaped. Oval, triangular. Bean shaped. Small spherical concentrically built.	Observable at pointed end. Observable on concave side. —			Occasional compound granules, 2-3 components.
13. French Bean.	<i>Phaseolus vulgaris</i> .	30-50 μ .	Rounded or oval.	Centric.	Fairly marked.	General, from hilum.	
14. Bean, Scarlet Runner.	<i>Phaseolus multiflorus</i> .	20-35 μ .	Rounded or oval.	Centric.	Not distinct.	General, radial from hilum.	Size differentiates from French Bean.
15. Colocasia esculenta.	—	10-55 μ .	Regular and oval.	Fairly distinct, at narrow end.	Only on inner part of granule, then wide zone with none.	—	
16. Millet, Dhurra (Durra, Dura).	<i>Sorghum vulgare</i> (Sudanese).	15-35 μ .	Rounded polygonal shape.	Centric.	Not visible.	Fissured, freq. stellate.	
17. Millet, Nigerian White Guinea corn.	" (Nigerian).						
18. Millet, Indian Jowar.	" (Intama).						
19. Millet, Shama.	<i>Panicum colonum</i> (India).	8 to 15 μ . Some up to 20 μ .	Polygonal or rounded polygonal.	Centric and punctiform.	Not visible.	Sometimes sl. fissured.	
20. Millet, Italian.	<i>Setaria italica</i> (India).	8-15 μ .	Rounded or polygonal.	Centric, fairly distinct.	Not visible.	Sometimes sl. fissured.	
21. Millet, Ragi.	<i>Elesine coracana</i> (India).	6-20 μ .	Polygonal.	Centric, sometimes faintly fissured.	Not visible.	Sometimes sl. fissured.	
22. Maranta (original Arrowroot).	<i>Maranta arundinacea</i> (West Indies, Jamaica, Bermuda, St. Vincent, and Natal).	13-70 μ . Chiefly 27-54 μ .	Similar to potato. Note size difference.	Sometimes centric, more often excentric.	Always visible, but not strong.	Hilum often fissured in form of double curve like flattened ω .	Always simple.
23. Maranta.	<i>Maranta nobilis</i> .	11-34 μ .	Simple.	Centric.	Only distinct after chromic acid treatment.	Radial after chromic acid treatment.	Compound granules observed very rarely. 2-5 small components.

TABLE XVI—(Concluded)

Name.	Source.	Granule Size	Granule Shape.	Hilum.	Striae.	Fissures.	Comments.
24. Mango.	<i>Mangifera indica.</i>	5-25 μ .	Mostly compound, very few simple granules.	Very distinct.	Easily visible.	—	—
25. Horse Chestnut.	<i>Aesculus hippocastaneum.</i>	Small 3-8 μ . Large 14-35 μ .	Round or elliptical. Simple and some compound. Simple and compound. Pear-shaped or conical, irregular.	Distinct and often fissured.	Concentrically striated. Distinct and excentric.	—	Both simple and compound in small. Both simple and compound in large. Compound consists of 1 large and 1 or 2 small.
26. Tacca (Tahiti or Williams Arrowroot).	<i>Tacca pinnatifida</i> and <i>T. Oceanica.</i>	25-45 μ .	Simple — elliptical, egg or pear-shaped.	Centric or only sl. excentric. Distinct.	Distinct.	—	—
27. Waxy Sorghum (Red Leoti).	—	6-30 μ . Chiefly about 15 μ .	Similar to maize.	Centric and distinct.	Indistinct.	Distinct and radial from hilum.	Red iodine coloration.
28. Waxy Maize.	—	5-25 μ .	Similar to common maize (p. 00).	Centric and distinct.	—	—	Red brown coloration with iodine.
29. Sweet potato.	—	10-25 μ . predominate.	Polygonal.	Centric and distinct.	Faint if any.	—	—
30. White Dioscorea.	<i>Dioscorea alata.</i>	Small—15-30 μ . long, 7-15 μ . wide large—45-90 μ . by 25-60 μ wide.	Simple, irregular, oval or elliptical or rounded triangular. Larger extremity of granule often truncated.	Distinct excentricity of 1/5-1/7.	Distinct.	—	Greyish yellow colour.
31. Yellow Dioscorea.	<i>Igname indien jaune.</i>	8-55 μ .	Much tissue present. Elliptical, egg, pear or heart-shaped, but do not appear truncated.	Not readily visible except in glycerol, is then distinct.	Fairly distinct and very numerous.	—	Intense greyish yellow to brown colour.
32. Red Dioscorea.	<i>Igname indien rouge.</i>	17-119 μ .	Parenchymatous tissue generally present. Granules have red colour. Like White variety but narrower.	Distinct. Excentric.	Distinct.	—	Dirty red powder. Colour of granules turns bright red with acid, blue with alkali.
33. Zanna (Florida arrowroot).	—	5-75 μ .	Hemispherical or dome shaped. Some	Not well marked when fresh.	Not well marked when fresh.	Radial fissures.	Mostly compound granules, 2-8 components.

It is most valuable to compare samples under examination with those of known origin, much more being learnt in this way and by practice than from any amount of description. A most complete set of photomicrographs of starches has been published by Reichart,³⁶ some 306 starches in ordinary and polarised light being shown, and the reader is referred to this work if unable to obtain genuine samples of starch for examination, but however good photomicrographs may be it is always highly desirable to examine samples of the genuine starches. A comparison microscope is very useful for this type of work especially if the microscopist is not skilled in starch examination. In addition, the reader is referred to the photomicrographs of modified and pasted starch published by Sjostrom¹³ and S. Woodruff.³⁷

The average buyer or user of starch is generally assured of the authenticity of his materials. He is then interested in the value, which is obtained by determining the moisture and other extraneous matter present, the latter often giving information on the manufacturing history of the sample.

Moisture.—The moisture-content of a starch is of importance, as the buyer does not want to pay for more water than is normally present in air-dry starch. In air-dry wheat starch the moisture-content is usually around 13 per cent., whilst that of potato is between 18 and 22 per cent. Should a greater percentage be present in the latter, the price should be adjusted so that moisture in excess of 22 per cent. is not paid for. Furlong⁷⁵ suggests a figure of 12·5 per cent. for moisture in superfine tapioca, this being the maximum limit. When determining moisture by finding the loss on heating, it must be borne in mind that most starches gel between 57° and 67° C., and thus it is advisable to keep the temperature at 40° C. for some hours until the greater proportion of the moisture has been driven off. The temperature may then be raised to 120° C. for 4-6 hours. The author has found it advantageous to add 5 ml. of absolute alcohol to every 10 gm. of starch taken, the time of drying thus being reduced.

Sprockhoff²⁷ gives the official German method in which 5 gm. of starch are heated for 1 hour at 50° C., and then for 3 hours at 120° C. He also describes a method requiring only 1 hour, claimed to be accurate to 0·2-0·4 per cent., in which 10 gm. are placed in a shallow dish that is suspended on a wire through the top of an oven and attached to one arm of a balance. After heating for 15 minutes at 90-100° C., the temperature is raised to 140-150° C. for 25-30 minutes, and the loss of weight determined.

Saare¹⁴ gives a rapid method for estimating moisture in potato starch which is claimed to be accurate to 0.5 per cent. : 100 gm. of starch in a graduated flask are made into a suspension with distilled water, the volume made up to 250 ml. at 17.5° C., and then weighed. If S represents the weight of the starch plus the water in the flask then the water-content of the starch is given by

the formula : per cent. water = $\frac{289.4 - S}{0.394}$. The weighing should be done as accurately as possible, as a difference of 0.1 in S represents a final difference of 0.25 per cent. water.

J. A. Radley has made use of the hygroscopic nature of absolute ethyl alcohol to determine the moisture-content of potato starch by finding the specific gravity of the supernatant liquid obtained by shaking up known weights of alcohol and starch; the results were in close agreement with those obtained by other methods. It is possible that the refractometer could be used with advantage in this method.¹⁵

T. H. Fairbrother and R. J. Wood²⁸ find that distillation with tetrachlorethane or carbon tetrachloride allows the moisture in flour to be estimated in 20 minutes with an accuracy of ± 0.5 per cent. They also confirm the claims to accuracy and speed of the Burton and Pitt method,²⁹ in which the moisture present is determined from its effect on the dielectric constant of the material under examination. Although their results were obtained with wheat flour these methods should be applicable to the determination of moisture in starches and dextrins.

It seems possible that more use might be made of the azeotropic mixtures which various solvents form with water for the determination of the latter. The few selected solvents below show properties which are suggestive for this work.

TABLE XVII

<i>Added Liquid A.</i>	<i>B. Pt. A.</i>	<i>B. Pt. of Azeotrope with Water.</i>	<i>Wt. per cent. of A.</i>
Benzene . .	80.2° C.	69.25° C.	8.83
Cyclohexane . .	80.75° C.	68.25° C.	8.33
Toluene . .	110.7° C.	84.1° C.	19.6

The greatest amount of water in any azeotropic mixture is probably that formed by 1-octanol which contains 99.4 per cent. water by volume or 90 per cent. by weight.

Using a pyridine solution of methyl magnesium iodide. T. Zerewitinoff¹⁶ has estimated the amount of methane liberated

by the addition of starch, and finds close agreement between the values obtained on vacuum drying by this method. J. F. Hoffmann and J. H. Schulze¹⁷ suspend the starch in a mixture of turpentine and toluene, distil off water and measure it. S. Maquenne¹⁸ noted that drying at 120° C. for 1 hour, followed by 2 hours at 100° C. in a current of dried air, gave results which were lower than those obtained by the usual methods, the difference being as large as 1 per cent. of the weight of sample taken.

Moisture determinations have been made by L. Sair⁸⁰ on 22 commercial starches and modified starches using distillation, vacuum-oven and air-oven methods and reasons for differences in the results given by the different methods are suggested. He concludes that the toluene distillation procedure and the vacuum-oven method at 100° C. are suitable reference methods. Rapid oven procedures involving temperatures as high as 140° C. he considers reliable with most starch products but not with acid-modified or hypochlorite-modified products which should not be taken above 100° C. It is interesting that this worker found that the sorptive power of modified starches decreases with increasing modification but that the sorbed water is held with equal, if not greater, tenacity than the water held by the original unmodified starch. This the author can confirm from his own experience on the subject.

In 1935, Karl Fischer introduced a complex reagent consisting of pyridine, methanol, sulphur dioxide and iodine which has a specificity for water. Fosnot and Haman have investigated the use of this reagent for moisture determinations of cereals and cereal products. The Fischer method can be completed within 10 to 60 minutes, depending on the time the material has to stand in contact with the reagent, whereas the oven methods require at least several hours. This is a useful saving in routine control. The time of contact between the material and the reagent required to give complete extraction of the water depends upon the physical condition of the sample particularly the particle size. The agreement with the oven method is good. Maize, starch and wheat flour only gave a fair agreement so that further work is required. Tables XVIII, XIX show the figures obtained. (See p. 336.)

A critical examination of a number of methods used to determine the moisture in potato starch has been carried out by W. L. Porter and C. O. Willits.⁸⁹ They used two types of mechanical convection oven viz. a Brabender moisture tester and a Precision floor model. The Brabender moisture tester (an air oven with forced circulation) has a balance incorporated in such a

TABLE XVIII

Moisture content of Maize Starch by Oven and Fischer methods.

<i>Statistical value.</i>	<i>No. of determinations.</i>	<i>Moisture content.</i>
Maximum	10	12·32
Minimum	10	12·14
Mean	10	12·22
Oven mean	2	11·60
Standard oven (single determination)	10	0·0

TABLE XIX

Comparison of Oven and Karl Fischer methods for Various Materials.

<i>Material.</i>	<i>Moisture Content.</i>	
	<i>Fischer.</i>	<i>Oven.</i>
Wheat flour	12·1	11·6 (8 hours)
Oat flour	8·1	8·1
Soya flour	6·1	5·9
Wheat gluten	7·0	7·0
Corn flakes	9·35	9·65
Barley	7·3	7·3
Wheat	7·1	7·0

manner that the sample can be weighed without removing it from the oven. The oven was regulated to different temperatures and the loss in weight was noted at definite time intervals until constant. With the Precision floor model several samples for each particular drying temperature were placed in the oven, one being removed after each time interval, so that repeated heating and re-cooling was avoided. A similar procedure was adopted with a table-model, gravity convection oven. Carter-Simon tests were made with a number of samples weighed at the same time, but passed through the oven at different rates so that the time of drying was varied. Tests in a Weber vacuum oven (< 5 mm. of mercury) were made in the same manner as with the mechanical convection oven. The loss of weight of potato starch recorded by the Brabender moisture tester becomes greater with successively higher temperatures, the rate of loss at each temperature being higher at the beginning and falling off rapidly until the weight is constant. The curves show that the total loss of volatile matter is dependent upon the temperature. At a high drying temperature a light brown discoloration appears in the time necessary to establish constancy of weight. This alteration does not affect the weight and determinations of the spectral reflectance and estimation of the colour given with iodine

by aqueous extracts showed, respectively, that no change in composition and solubility occurred before the constant weight period. With drying at 180° C. appreciable decomposition, indicated by further loss in weight and formation of erythro-dextrins, occurred only when heating was continued for 4 hours after the attaining of constant weight. Any method for the determination of moisture based on the steep portion of the isothermal curves showing the relation between loss of weight (ordinate) and time (abscissa) is subject to considerable error produced by relatively small time differences. This may account for the inconclusive data reported in the literature of moisture-content of potato starch, since most of the standard methods specify conditions represented by points on the steep portions of the curves. A more closely reproducible method would consist in the use of a temperature indicated on the flattest portion of the curve and a time long enough to ensure constancy of weight. With the Brabender moisture tester the method would involve heating at 135° - 145° C. for 30-60 minutes to the constant weight. Now that this basic method has been established it should be possible to employ any other method that will duplicate these moisture values within the limit of error of the specific procedure. With potato starch dried in a gravity convection oven at 100° C. for 24 hours the loss in weight never quite reached the value obtained in the mechanical convection oven at 100° C. nor was the drying so rapid. In neither form of oven did the loss reach that established by the basic method. Vacuum drying at 5 mm. of mercury at 80° C. gave a value in close agreement with that of the basic method, constant weight being reached in 22-24 hours. Vacuum drying at 100° C. gave a slightly higher value with constancy in 5 hours. Drying at 100° C. by any of the other methods gave lower values. At 135° C. the air drying methods used, with the exception of the Carter-Simon method, gave results comparable with those of the basic method. At higher temperature (150° C.) slight decomposition occurred. Quick approximations can be made, however, by heating at such a temperature for a time that will give a loss of weight comparable with that of the basic method (e.g. the Carter-Simon moisture test) which is operated at 155° C. for 15 minutes), but heating must be stopped at the end of the specific time. Distillation methods gave results of the same order as those of the oven methods, and generally as the temperature of distillation was raised the amount of water obtained increased. The lower-boiling liquids (carbon tetrachloride and toluene) gave low results: Xylene and tetrachlorethane gave results agreeing with those of the basic method, tetrach-

lorepthane having the advantage that the starch floated on the top. The Karl Fischer chemical method for determination of moisture gave low results with potato starch. According to the method employed under conditions that rendered the results comparable with those of the basic method, the values found for the moisture-content of the potato starch used ranged from 16.33 to 16.58 per cent.

Mineral Matter.—The determination of mineral matter will often show whether a starch has been 'chemicalled,' as well as the inclusion of sand or dirt: 5 gm. are ignited in a dish in a muffle furnace until the ash is white or very light grey in colour. A high-grade potato starch will have an ash-content of about 0.2-0.4 per cent. on the dry starch, whilst 0.15 per cent. is generally found for wheat or maize starches, but the figures may rise as high as 0.5 per cent. if it has been 'chemicalled'. Low quality tapiocas generally have a high ash-content of a brownish colour, whereas the ash of high-grade tapioca is less and is white in colour. The amount of ash, however, cannot be used as a guide to quality.

W. Völksen⁷⁹ suggests taking 15 gms. of starch, dextrin, etc., ashing in a platinum dish in an electric muffle furnace at 900° C. for 30 minutes, after which time, if particles of carbon are present, a small amount of 10 per cent. ammonium nitrate solution is added followed by a further short addition. The dish is weighed immediately it has cooled to room temperature. More accurate results are claimed by this worker, together with a shorter ashing time, if the sample is wet with 6 c.c. of alcoholic magnesium acetate (1.61 gm. in 100 c.c. of 95 per cent. ethanol), in which case 0.02 gm. must be subtracted from the ash.

H. Tryller¹⁹ considers that the presence of calcium in the mineral matter may be ascribed to the washing water, but it must certainly be borne in mind that some factories use calcium bisulphite in the manufacture of the starch and there is a possibility of this being a contributory cause of the presence of calcium. With certain 'prepared' starches the chemicals mentioned in the various sections should be looked for, due regard being paid to the behaviour of the starch in use which will give an indication of substances likely to be present.

When determining phosphorus in starch the results are sometimes low when incineration is employed. G. Steinhoff⁶⁷ overcomes this by destroying the organic matter with concentrated nitric acid containing 5 per cent. potassium permanganate. This is later removed with hydrogen peroxide and the phosphorus precipitated as phosphomolybdate. This is dissolved in 1 per cent. ammonia, the excess of this being fixed with neutral formal-

dehyde, and then titrated with 0.1 N caustic against phenolphthalein.

Fat.—T. C. Taylor and J. M. Nelson,²⁰ considered that a small amount of the fat contained in maize starch is in combination with the starch and not removable by solvents, a conclusion which has since been proved wrong (*v.i.*), however, on hydrolysis this fat is set free and appears as palmitic acid, etc. Further work by Taylor and L. Lehrman²¹ has showed that the fatty matter has approximately the following percentage composition: palmitic acid 24, oleic acid 40, linoleic acid 36. The above workers find that the percentage of fatty matter in maize starch is approximately 0.5, in rice starch 0.83, in sago starch 0.11, and in cassava starch 0.12.

Thus, for some years a distinction was made between the so-called 'combined fatty acids' and the free fatty acids, the latter being readily removable by extraction with ether or petroleum ether in a Soxhlet apparatus, the former requiring acid hydrolysis of the starch before being set free. It is now known that all the fat in the granules is but loosely held, the major portion being removed from intact granules by a Soxhlet extraction with methanol for 10 hours. When the granules are disintegrated a short extraction gives complete and easy removal.⁹⁰

K. A. Clendenning and D. E. Wright⁹¹ have carefully prepared pure samples of starch according to the methods of various workers.⁹²⁻⁹⁵ The fat content was determined by the acid-digestion method and it was found that the fat content of the waxy starches was consistently lower than that of the corresponding non-waxy cereal starches. Oat starches had by far the highest fat content averaging 1.2 per cent. The fat content of legume, bulb and tuber starches was low but measurable.

Determination of Nitrogen and Protein.—The proteins in a given sample of starch may be calculated by carrying out a Kjeldahl nitrogen determination and multiplying the figure for nitrogen by 6.25, except in the case of wheat starch where Wright and Clendenning⁹¹ recommend the use of the factor 5.7.

The following represent typical results of the analyses of various starches, the lower figures representing the amounts in a commercial superfine quality. (See Table XX on p. 340.)

It is of interest to examine the figures of Clendenning and Wright for moisture, ash, fat, protein and specific rotation obtained on laboratory-prepared samples of starch. Table XXI gives the figures taken from their paper. (See p. 341.)

Thus the various types of starch show consistent differences in the non-starchy solid fractions, but differences between samples

TABLE XX

<i>Component.</i>	<i>Wheat.</i>	<i>Maize.</i>	<i>Tapioca.</i>	<i>Potato.</i>
Moisture	11-15 per cent.	10-15 per cent.	9-18 per cent.	18-22 per cent.
Protein	Less than 0.5 per cent. in good grades.	0.1-0.2 per cent. Inferior grade, 1.0 per cent.	0.15-1.0 per cent.	Nil.
Ash	0.25 per cent. or below.	0.1-0.2 per cent. in 'unchemicalled'; 'chemicalled' 0.3-0.5 per cent.	0.1-0.8 per cent.	0.2-0.3, not over 0.5 per cent.
Fat	0.15 per cent.	0.5-0.75 per cent	0.1-0.4 per cent.	Nil.

of the same kind, carefully prepared under similar conditions, in this respect are, for the most part, very small. Millet and commercial rice starches have the highest protein contents, and these, together with grain sorghum, are also highest in ash. Waxy cereals, legume, root, bulb and tuber starches are low in fat while the non-waxy cereal starches have high fat contents, oat starch exceeding all others in this respect.

Acidity.—The acidity of starches is sometimes determined and a qualitative test is carried out by spreading a small heap of starch on a plate and moistening it with two or three drops of purified litmus solution.

For a quantitative estimation, Saare shakes 25 gm. of starch with 25-30 ml. of water and titrates with N/10 caustic soda solution against phenol phthalein. Under these conditions he classes as 'technically free' those requiring less than 3.75 ml. of N/10 alkali, whilst those requiring 5.0, 5.0-8.0, and over 8.0 ml. are classed as faintly acid, acid, and strongly acid, respectively. The low acidity required in tapioca starch has already been mentioned on p. 312. J. Mayrhofer has pointed out the advantages of electrometric titration.³⁰ L. Pickens and D. T. Englis point out that pH value and titrable acidity are of little value in classifying starches.⁷¹

According to H. Tryller,²² the acid reaction is due to several components, such as sulphur dioxide, and propionic acid in inferior starch, but is chiefly related to the amount of amylophosphoric acid present as hydrolysable salts (see Vol. I). The results obtained by titration are often not a measure of the acidity of a sample, since a starch containing a small amount of a strong acid would be more acidic yet give a lower titration value than

TABLE XXI

<i>Sample.</i>	<i>H₂O</i> %	<i>Ash</i> %	<i>Fat</i> %	<i>Protein</i> % (N × 6·25)	<i>Specific</i> <i>Rotation</i> <i>Degrees.</i>
Wheat Marquis	9·21	0·18	0·57	0·21	202·3
" Thatcher	9·33	0·15	0·51	0·21	202·7
" Garnet .	11·19	0·20	0·53	0·22	202·5
" Dicklow .	11·03	0·28	0·57	0·29	202·8
" Blanca .	11·93	0·24	0·61	0·18	203·2
" Ontario soft winter	9·07	0·14	0·48	0·17	202·3
" Mindum .	12·27	0·21	0·59	0·23	202·7
" Kharkov .	11·27	0·24	0·55	0·18	202·6
" Jones Fife	11·06	0·27	0·58	0·19	203·1
Maize . . .	11·36	0·05	0·62	0·29	202·3
" . . .	9·12	0·05	0·64	0·37	202·9
" . . .	10·44	0·05	0·71	0·37	202·9
" . . .	11·29	0·07	0·72	0·39	203·2
" . . .	9·08	0·07	0·77	0·27	203·4
Waxy Maize	10·50	0·05	0·20	0·26	202·3
Barley . . .	9·53	0·14	0·73	0·18	203·5
Waxy Barley	9·26	0·12	0·43	0·27	202·4
" " . . .	13·95	0·23	0·30	0·09	202·5
Rye . . .	9·53	0·14	0·47	0·18	202·8
Oat . . .	10·78	0·10	1·20	0·31	202·6
" . . .	9·46	0·20	1·17	0·31	203·1
Rice . . .	10·07	0·59	0·66	0·46	202·8
" . . .	10·17	0·28	0·87	0·56	203·8
" . . .	11·95	0·65	0·68	0·51	202·7
" . . .	11·21	0·33	0·45	0·14	202·6
Waxy Rice	9·95	0·36	0·12	0·54	203·1
" " . . .	10·19	0·15	0·10	0·06	202·3
Grain Sorghum	12·91	0·41	0·72	0·14	202·3
Waxy Sorghum	10·23	0·32	0·39	0·34	202·3
Millet . . .	10·46	0·53	0·91	1·28	201·4
Buckwheat	15·88	0·19	0·53	0·32	203·4
Pea . . .	10·84	0·22	0·18	0·36	199·4
Bean . . .	14·15	0·20	0·25	0·30	200·2
Lima Bean	9·73	0·12	0·17	0·19	200·5
Potato . . .	12·88	0·30	0·18	0·17	204·8
" . . .	14·80	0·32	0·12	0·11	203·8
" . . .	14·84	0·34	0·11	0·08	203·7
" . . .	12·18	0·32	0·11	0·08	203·9
" . . .	10·13	0·29	0·13	0·18	204·4
" . . .	9·15	0·40	0·12	0·10	203·7
" . . .	12·42	0·33	0·15	0·08	203·4
Sweet Potato	10·19	0·20	0·13	0·07	203·3
" " . . .	10·43	0·21	0·12	0·07	203·5
Arrowroot	8·94	0·12	0·15	0·08	203·6
" . . .	10·49	0·16	0·16	0·09	202·9
Tapioca . .	10·13	0·10	0·27	0·09	203·0
" . . .	10·17	0·08	0·27	0·14	202·6
Easter Lily	8·74	0·37	0·27	0·04	203·9

one containing a higher proportion of weaker acids. If it is necessary to neutralise the starch at some subsequent stage of

processing the latter figure is important, but for determining the quality of the starch C. Schéele³¹ considers the *pH* value of the starch is of most value, and gives a method of determining this. A complete picture would, of course, be obtained by determining the electrometric titration curve which would give all these figures in one diagram.

For starches to be used in foodstuffs, the amount of SO₂ present should be determined, and should not exceed 100 parts per million as laid down in the Food and Drugs Acts.

Pentosan Content of Wheat Starch.—Baker, Parker and Mize⁹⁸ have separated the starch and gluten of wheat flour by the ordinary gluten working technique, the starch being collected by centrifuging. The top or 'amylodextrin' layer was separated from the prime quality starch in the lower layer and purified by successive washing and centrifuge treatments. Upon analysis the 'amylodextrin' fraction was found to contain 14·0 per cent. of pentosans using the Schmidt-Nielson and Hammer method.⁹⁹ The prime quality starch gave a content of 0·4 per cent. pentosans by this method. These authors concluded that the wheat starch granules were all coated with insoluble pentosans, the higher pentosan content of the 'amylodextrin' fraction being attributed to the smaller average particle size and the concomitant greater surface area of this fraction as compared with the prime quality starch fraction.

Clendenning and Wright⁹¹ find the same differences between the two fractions. They found that the phloroglucide of the second distillate from prime quality wheat starch was completely soluble in 95 per cent. ethanol. Using the Hughes-Acree bromine oxidation method¹⁰⁰ or phloroglucinol precipitation¹⁰¹ for the estimation of 'furfural', dextrose gave apparent pentosan contents of the same order (0·4 per cent.). Evidently with large samples of starch redistillation from saturated sodium chloride does not ensure complete removal of hydroxy-methyl-furfural as has hitherto been assumed.

Gelling and Water-holding Power.—The gelatinising power and the degree of tenacity with which a starch paste retains its moisture is a measure of its superiority, the lower grades going thin after a short time whilst good grades give a paste which retains its firmness for a very much longer period. This property may be measured in two ways; the first described below is due to Schreib, and the second is a method used in a number of factories.

Schreib's Method.—Four grams of starch are suspended in 50 ml. of cold water and heated to boiling with constant stirring.

When the liquid begins to boil the flame is removed and the stirring continued. The starch should not be boiled for longer than one minute, and when cold the jelly should not flow when the container is inclined.

In the second method, which utilises the principle of capillary attraction, 16.6 per cent. starch pastes (dry weight basis) are made with the samples in dishes of the same diameter. When cold and set the paste is transferred to a filter paper, still keeping it in the moulded form, and put aside in a place free from draughts. All the samples should be made up under identical conditions of temperature, stirring, etc. The size of the water-rings formed on the papers is examined after 1, 12, and 24 hours; the sample showing the largest ring is graded as the worst starch and that with the smallest as the best.

Direct determinations of viscosity on starch pastes do not give very concordant results, as the method of preparation can play a big part.⁴¹ Instead of gelatinising the starch in water, W. F. A. Ermen²³ swells 1.25 gm. of starch in 245 ml. water, containing 1.5 gm. caustic soda, makes up to 250 ml. when swelling begins, and after several hours determines the viscosity of the solution with a Redwood viscometer. The results clearly indicate differences in the manufacturing history of samples, and different starches are readily distinguished from one another. A number of other methods, useful in factory control or routine examination of samples being purchased, are discussed in Chapter 19, especially in the section dealing with the rigidity of starch pastes.

W. Ekhard³² has described in full an apparatus for determining the adhesive power of starch pastes. He takes 9 gm. of air-dried potato starch, makes it into 200 gm. of mucilage with water of known temperature, and sinks a 22 mm. disc in the paste. After 24 hours the weight required to withdraw the disc from its fixed depth in the cold mucilage is determined. A similar method is used by O. Saare.⁴² A. Bintz and T. Marx⁵³ find Saare's method applicable to rice but not to potato and wheat starches. H. Cappenberg⁵⁴ compares the time to pull a sphere, under a pull of a known force, through a given thickness of paste. These methods give results which are seriously affected by very slight variations in the method of making the paste.³³ Sprockhoff³⁴ criticises these methods and adopts viscosity as a criterion of quality, using 0.4-1.0 per cent. solutions. Schulz and Parlow³⁵ also use the Sprockhoff viscometer to judge the quality of the starch and have examined starch from frozen potatoes and starch which has been frozen, to determine the effect of this treatment

on the tenacity of the pastes made from the two starches. Reference, however, should be made to the chapter on Physical Properties, in which the rigidity of starch pastes is discussed and to Chapter 19.

Dextrinisation Test.—When this test is carried out the various purchasers will no doubt have their own modifications which give them information as to the suitability of the material for manufacturing certain grades of dextrins in which they are interested. For cassava starch J. R. Furlong⁷⁵ suggests the following test: to 10 gm. of the starch in a mortar is added 0.2 c.c. of dilute hydrochloric acid (3.4 per cent. W/W) and 0.2 c.c. of dilute nitric acid (3.0 per cent. W/W) and the mixture well rubbed with the pestle until the acid is homogeneously distributed. The acidified starch is stored overnight in an open beaker on the laboratory bench after which it is spread in a thin layer on filter paper and dried in an oven at $35^{\circ}\text{C.} \pm 3^{\circ}\text{C.}$ for 3 hours. The paper and mixture is then transferred to an oven and roasted at $155^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$ for 1 hour after which there should be a distinct colour change to a cream, buff or pale yellow and the powder should be soluble in water, either on shaking in the cold or on warming slightly. To this solution, adjusted to about 10 per cent. in strength is added 2 to 3 drops of a 1 per cent. iodine solution when a well-dextrinised product will give a reddish brown colour, unconverted starch gives a blue colour.

The Alkali-Labile Value.—A technique which may prove of value in routine and factory examination of starch, modified starch and dextrin has been elaborated by T. C. Taylor and his co-workers.³⁸⁻⁴⁰ It depends on the fact that these substances contain a portion termed 'alkali-labile' which is readily acted upon by alkali. Various pre-treatments of starch bring about changes in the amount of this alkali-labile portion, and Taylor's method, whilst giving empiric values, is precise, semi-micro and readily duplicated, providing the technique laid down is followed rigidly. The method detects changes which cannot be determined by viscosity tests, iodine reaction, specific rotation, or initial reducing value determinations. Tests should be done in duplicate at least and are carried out as follows⁴⁰:—

50.0 mg. \pm 0.1 mg. of starch are weighed into a Pyrex test tube, 8" \times 1", and 10 ml. of 0.1 N NaOH added. The tube, loosely stoppered, is floated on a boiling water-bath for 1 hour, after which it is cooled for 30 seconds under running cold water. 10 ml. of 0.1 N HCl being added immediately it is removed from the cold water and the contents of the tube well mixed by thorough shaking. The mixture is transferred to a 250 ml.

Erlenmeyer flask, the tube being washed twice with 10 ml. distilled water and the washings added to the flask.

Two drops of nitrazine yellow solution are added and the liquid is neutralised with 0.1 N NaOH. Five ml. of the alkali are then added, followed immediately by 5.0 ml. of 0.025 M standard iodine solution; the last three operations should be carried out within 3 minutes. The flask is kept at 25-30° C. for 45 ± 1 minute in the dark, and then 5.0 ml. of conc. HCl added, mixed well by shaking and immediately titrated with 0.025 M thiosulphate solution. If the back titration is less than 3 ml. the resulting alkali-labile value will be low and 7 ml. instead of 5.0 ml. of iodine solution should be added for the oxidation of a second sample, so that a reading of at least 3 ml. is obtained in the back titration with thiosulphate. One hundred times the number of milligrams of iodine consumed divided by the weight of the sample in mgs. gives the alkali-labile value.

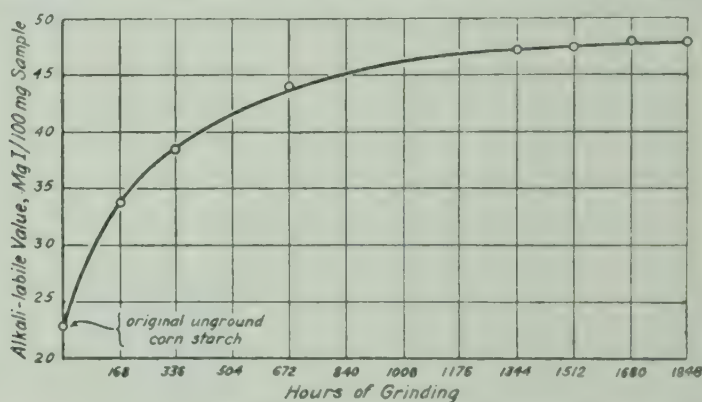
Pastes may be precipitated with acetone-free dry methyl alcohol after which the alkali-labile value of the carbohydrate material may be determined. If the paste contains no electrolyte the addition of a few drops of 0.1 N BaCl₂ greatly assists the precipitation; free chlorine, hypochlorous acid, peroxides, borax or sulphur dioxide should be absent, as these absorb iodine. Fig. 5:19 in Vol. I shows the connection between the alkali-labile value and time of grinding a starch.

If the long chains of glucose units forming the starch molecule are parallel and co-ordinate links exist between the H of the OH groups of some chains and the O bridges of others as has been suggested (see Vol. I), the free aldehyde groups at the end of the chain, although primarily chemically free, might be protected by a dovetail-like fitting end to end of the bundles of parallel-bound chains. Disassociation of the co-ordinately-linked chains from one another would make the aldehyde groups available whilst hydrolytic scission of glucosidic linkages would give shorter chains and consequently new aldehydic groups. Taylor and Keresztesy⁴⁰ think the great increase in alkali-labile value in making soluble starch by dry-grinding (see Fig. 16:1), or by the Lintner acid-process, is due to the terminal aldehyde exposed by disassociation of the chains, whereas the slower hydrolytic breakdown of the glucosidic links is responsible for the fairly steady rate of fall ultimately attained.

A good grade, commercial air-dry maize starch gives an alkali-labile value of about 22, tapioca starch 14, a thin-boiling starch 60, and a yellow dextrin 20. The method should be of value in examining oxidised and acid-treated soluble starches.

M. Samec and B. Škerl⁴⁸ have studied the dependence of alkali-labile value on the length of boiling and temperature to differentiate between erythro- and amylo-substances. Native and partially attacked starch gave quite different results. The fractionation methods previously employed by these workers, e.g. pressure cooking, electro-dialysis, coagulation by freezing or by ageing, caused no structural changes as judged by alkali-labile value. They consider that a large number of starches can be characterised by this value.

T. J. Schoch and C. C. Jensen⁶⁰ have devised a simplified alkalimetric method to estimate the relative hydrolytic degradation



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FIG. 16:2

of starch. They consider that Taylor's alkali-labile value is liable to variations at the hands of different workers, especially where the starch has been precipitated by solvents, as the latter are tenaciously retained even on prolonged drying.

Schoch and Jensen digest 0.5 gm. of starch (calculated on a dry basis) with sodium hydroxide. The starch, which should pass a 60-mesh sieve, is introduced into an eight-ounce flask and shaken with 10 ml. of water until suspended, 25 ml. of 0.4 N sodium are added, taking care to agitate the contents of the flask so as to obtain uniform gelatinisation of the starch, followed by 65 ml. of hot distilled water. The flask is closed with a bung carrying a bunsen valve and immediately placed in a vigorously boiling water-bath. After heating for exactly 60 minutes the flask is placed in cold water and 50 to 75 ml. of cold distilled water are added to the contents of the flask to halt the decomposition. The liquid is then titrated against thymol blue to a yellow end-point with 0.2 N sulphuric acid. With highly coloured compounds the titration is carried out to a pH value of 8, using a glass electrode. The alkali number is calculated as (ml. of

acid to titrate blank—ml. of acid to titrate sample) \times normality of acid $\times 10 \div$ weight of sample on dry basis.

Close adherence to the above procedure is recommended. Should the starch product contain added acid or alkali, sufficient to affect the alkali number, 1 gm. of the product is gelatinised and titrated with alkali or acid against thymol blue, correcting the alkali number for this titre. With cold-swelling products the sample should be introduced into a perfectly dry digestion flask and wetted with 1-2 ml. of benzene; 25 ml. of 0.4 N sodium hydroxide solution are then added followed by 75 ml. of hot water. In this way complete dispersion without the formation of lumps is obtained.

Commercial corn and wheat starches have consistently higher alkali numbers than those of the common tuber starches. Schoch and Jensen find the following values: tapioca, 5.9-6.9; potato, 5.7-6.9; rice, 6.7-7.5; wheat, 9.7-11.5; maize, 9.8-12.1; maize (specially prepared by non-aqueous steeping), 10.6, 11.4.

By leaching at temperatures just below the gelatinising point raw corn starch gave a minor fraction of soluble carbohydrate possessing a high alkali number (35.9). The insoluble residue had an alkali number, 8.8, and the raw starch, 11.2.

By fractionation with cold water a typical acid modified thin-boiling starch was found to be heterogeneous in character. The initial thin-boiling starch gave a value of 44.1, the cold water soluble fraction 50.6, and the insoluble residue 36.9 for the alkali number.

With increasing degree of acid conversion the alkali number rises progressively in thin-boiling starches, e.g. 20-fluidity, 14.5; 40-fluidity, 15.0; 60-fluidity, 15.7; 75-fluidity, 20.7; 90-fluidity, 41.5; white dextrin, 25 per cent. cold water soluble, 56.3; white dextrin, 65 per cent. cold water soluble, 62.6; Lintner's soluble starch, 66.4.

British gums and yellow dextrans show alkali numbers only a little higher than that of raw corn starch, e.g. British gum, 17.5 per cent. soluble, 16.5; British gum, 80 per cent. soluble, 15.6; gum, 85 per cent. soluble, 16.3; dextrin, acetic acid conversion, 98 per cent. soluble, 16.4; yellow dextrin, nitric acid conversion, 85 per cent. soluble, 19.9; yellow dextrin, hydrochloric acid conversion, 97 per cent. soluble, 23.0. The alkali numbers bear no relation to viscosity or solubility. With oxidised starches the alkali number is generally lower than that of the raw corn starch. Alkali lability, however determined, must not be construed as a quantitative evaluation of aldehyde content, but merely as an empirical index of hydrolysis.

Potentiometric Measurement of Iodine Adsorption.—The reaction with iodine has been made the basis of a quantitative method for the determination of amylose. The iodine activity has been measured potentiometrically by Bates, French and Rundle.¹⁰² When iodine is added to an amylopectin solution the iodine activity rises rapidly. Upon adding iodine to an amylose solution the iodine activity of the solution remains constant as long as complex formation can take place. When all the amylose has been used up and no more is available for complex formation with the iodine the iodine activity rises with the addition of further iodine as it does for water alone. The inflection point can be obtained potentiometrically and the amylose content of different starches can be estimated by taking the quantity of iodine bound by Kerr's crystalline amylose^{103, 104} as standard. The figures obtained by this method for the amylose content of various starches are given below:—

<i>Starch</i>	<i>Amylose %</i>	<i>Starch</i>	<i>Amylose %</i>	<i>Starch</i>	<i>Amylose %</i>
Waxy rice .	o	Tapioca	17	Corn	28
Waxy sorghum	o	Rice	17	Sago	27
Waxy corn .	o	Banana	20.5	Wheat	24
Waxy barley	o	Potato	22	Lily bulb	34

No evidence can be found for compounds of intermediate properties. Amyloses from different starches are not identical in their behaviour with iodine; for example, the iodine activity necessary for complex formation is distinctly different. In general it has been found that the lower the iodine activity necessary for complex formation, the longer the starch chain. The results indicate that the heterogeneity of chain lengths within a given amylose is fairly small, or at least less than that between amyloses from different sources. We cannot infer, however, that the amylose from any starch source¹⁰⁴ is truly homogeneous as to chain length. The differences in the chain lengths of the various amyloses as shown by the iodine titration are also indicated by the results of viscosity measurements.

The above workers dissolve 0.01 to 0.04 gm. of starch in 10 c.c. of 0.5 N potassium iodide. When dispersal is complete the mixture is diluted with water, made neutral to methyl orange by the addition of hydriodic acid and then diluted to 100 ml. Thus the final solution is one of starch in 0.05 N potassium iodide. This solution should be slightly acid and they titrate it with 0.001 N iodine solution in a Leeds and Northrup type K potentiometer cell in conjunction with a normal calomel cell and bright platinum electrode. With well-dispersed starch equili-

brium is reached in 2-5 minutes after the addition of 1 ml. of the iodine solution. When the change of potential near the end of the interval takes place at a rate exceeding a few tenths of a millivolt per minute, more time is allowed between successive additions of the titrating solutions. Any galvanometer permitting adjustment of the potentiometer within 0.1 mv. may be used. The inflection in the curve, potential v. ml. iodine solution added gives the end-point of the titration. Other work in the paper by Bates, French and Rundle indicates that amylose will bind a given amount of iodine, depending on the chain length of the amylose, to form a complex and when the iodine exceeds this amount it is adsorbed onto the complex. In the case of amylopectin adsorption alone accounts for all the iodine taken up.

Amylopectins from different starches do not behave alike in the iodine titration although the results with any one amylopectin are quite reproducible. This appears to be due to the variation of the degree of branching met with in the different amylopectins. We would appear to have, in this method, the basis of a technique for identifying the starch used in making a starch paste or for making products in which the granule identity is lost in the process, since the more highly branched the amylopectin the lower its characteristic affinity for iodine. The next step in evolving such a technique would be the determination of the degree of homogeneity of the amylopectins from various sources. Since each amylopectin has a characteristic degree of branching, distinguishing it from others, it appears that the degree of branching is a fairly specific property of any one amylopectin. Meyer, Bernfeld and Press¹⁰⁵ attempted to find a pattern for the branching based on the varying digestibilities of different amylopectins. There may be some connection between the above observations and the characteristic colours given by iodine on the preparations obtained by Giri and Bhargava¹¹ (see p. 318) by the action of different amylases on various starches, the degree of branching determining the mode and extent of attack of the amylases and the adsorptive capacity of the final products. The inhomogeneities of various amyloses appear small and different potentials for complex formation are obtained for amyloses from different sources. Although these are small they are real, reproducible and beyond experimental error. Bates, French and Rundle titrated mixtures of maize and potato amyloses and obtained clearly defined breaks in the titration curve corresponding to the difference in iodine potential necessary for maize and potato amylose-iodine complex formation. This demonstrates that, in the case of these two amyloses at least, the inhomogeneities

of the two amyloses are not so great that they overlap each other.

The Examination of Modified Starches.—With these products it is generally desired to characterise them either for use or for matching purposes. Oxidised starches are invariably whiter in colour than acid-treated starches, and a microscopical examination will at once determine the raw material used. In use the most important property is the viscosity, but in endeavouring to characterise a starch for matching purposes a number of drawbacks are encountered in viscometric determinations. Some soluble starches made by acid treatment are not washed free from acid or the acid is incompletely neutralised, and this leads to a rapid fall in the initial viscosity on heating the solution. Solutions of soluble starch are also sensitive to the presence of impurities and electrolytes and to mechanical treatment. Highly modified starch swells before dissolving and must be heated to complete the dispersion, and such heating brings about further modification.

In spite of these drawbacks, viscometric methods are employed for the examination of these products, together with the reducing value by the method of W. A. Richardson, Higginbotham and Farrow.⁴⁵ With potato, maize, and sago starches which have been modified by hot acid treatment followed by neutralisation, these workers find that the degree of modification is accurately measured by the reducing value (R) which does not, however, indicate the degree of modification of oxidised starches or those treated in the granular state with acids. Starches in these two classes are washed free from reagent after modification, and such washing removes the water-soluble reducing substances.

F. F. Farley and R. M. Hixon⁸⁴ describe a much simpler method than that of Richardson and co-workers. They noticed that when measuring the reducing power of a series of starches by the Gore and Steele⁸⁵ modification of the Hagedorn and Jensen⁸⁶ ferrocyanide method the apparent maltose equivalent of the more soluble products when converted to milligrams of copper gave values equal to the copper numbers obtained by the longer method of Richardson *et al.* For raw starch and very slightly solubilised starch, high values were obtained by the Gore and Steele method attributable to the visible entrapment in the starch of iodine which was very difficultly released for measurement in the thio-sulphate solution.

Martin and Newton⁸⁷ avoided this difficulty when determining maltose in maltose-starch mixtures by using Hassid's ceric sulphate titration.⁸⁸ Farley and Hixon, therefore, oxidise the sample with excess potassium ferricyanide and the ferrous ion produced is titrated after 15 minutes at 100° C. with ceric sulphate. The

method gives the same results in the starch and dextrin range, but not in the range of sugars, as that of Richardson *et al.* The reducing power increases with increasing conversion of starch products except for the electrolytically oxidised starches, which, because of the method of oxidation and washing, have values equal to or lower than those of raw starches. The method can be used to follow the conversion by both acid and alkali of starch to thin-boiling starches, Gore starches or dextrans formed by acid or alkaline catalysts. Table XXII shows the results obtained.

TABLE XXII

Reducing Power of Starches and Starch Products.

Product.	Rcu Mg./gm.
Pearl Starch (Control)	6.8-7.9
Commercial Maize Starches	7.7, 9.4, 10.1, 11.2, 11.6
Waxy maize starch	9.0
Thin boiling starch, 40 fluidity	6.5
" " " 90 "	27.2
Chlorinated starch, 2.5% chlorine	14.9
" " " 5.0% "	32.9
Electrolytically oxidised starches	6.8, 3.0, 6.3, 4.5, 7.5
Alkali dextrin A	10.5
" " B	33.0
" " C	71.0
Acid " A	12.0
" " B	25.5
" " C	39.0
Gore starch, 5 hour conversion	19.6
" " 42 " "	61.6
" " 96 " "	120.0
Maltose	1900
Glucose	2800

Interesting results in the examination of soluble starches have been obtained by Richardson,⁴⁶ using the following technique. A suspension of starch in cold water is poured into sufficient boiling water to produce a 2.5 per cent. solution which is heated for 1 minute and then cooled. After passing through a homogeniser the concentration is determined by the dichromate method.⁴⁵ To 10 ml. of this solution is added 15 ml. of a 50 per cent. calcium thiocyanate solution, a control solution of 30 gm. of this salt in 100 ml. of water also being prepared. Ten millilitres of each solution are used in separate U-tube viscometers (cf. Higginbotham and Richardson⁴⁷), and n , the viscosity of the starch solution relative to the control, is determined at 25° C. \pm 5° C., and if c is the concentration of the starch in gm. 100/ml., the 'thiocyanate viscosity' (TV) is given by the quantity $(\log n)/c$. Where c is between 0.6 and 1.0 per cent. TV is independent of c , and so long as c is known accurately it is unnecessary to adjust it

to a given value. TV runs parallel to R for acid-modified neutralised starches, and, like this value, may be used as a satisfactory index of the degree of modification. TV is preferable to R as the modification index for oxidised and acid-treated, washed starches (*vide supra*).

With unmodified or lightly modified starches TV is very sensitive to mechanical treatment, but this effect diminishes with increase in the degree of modification until, when R exceeds 40, homogenisation is superfluous. With oxidised starches, however, R may be lower than for an acid-treated, neutralised starch of the same degree of modification and may not, therefore, need homogenisation even when R is less than 40.

M. I. Knyaginichev⁵⁹ uses 30 or 50 per cent. sodium salicylate solutions containing 0.2 gm. of starch per 100 ml. for the examination of starches. He finds the viscosities for the different starches and modified products are unaffected by time and often differ more than the corresponding aqueous solutions. Incidentally, this worker finds that the larger granules give more viscous pastes than do the smaller granules.

Determination of Carboxyl Groups.—L. H. Elizer⁸² has developed a method for the determination of carboxyl groups in commercial starches modified by oxidation. Briefly a weighed sample of the starch is left in contact with a solution of silver o-nitrophenolate for 18 hours and the clear, supernatant liquid is then titrated with ammonium thiocyanate. A more convenient method, which gives slightly higher values, depends on the use of copper acetate and the clear supernatant liquid is titrated iodometrically. This method can be varied to give a satisfactory routine procedure by following the copper acetate treatment by the addition of potassium ferrocyanide solution to the supernatant liquid and comparing the colour produced with standards.

E. K. Gladding and C. B. Purves⁸³ estimate the carboxyl groups present in oxystarch and oxycellulose by treatment with hydroxylamine hydrochloride to form the oxime and titrating the liberated hydrochloric acid with standard alkali. Condensation occurs within 1.5 hours with oxystarch, the carboxyl groups being classed as a 'fast' type.

By the judicious use of the microscope and the determination of the reducing value R, the thiocyanate viscosity and the alkali-labile value the previous history and degree of modification of a sample of soluble starch may be determined sufficiently accurately to enable it to be matched for factory production.

REFERENCES

1. K. FREUDENBERG, *J. Soc. Chem. Ind.*, 1931, **50**, 288T.
2. H. N. HAWORTH, *ibid.*, 1934, **53**, 1059.
3. G. BLUNCK, *Zeit. Nahr. Genussm.*, 1915, **29**, 246.
4. E. UNNA, *ibid.*, 1918, **36**, 49.
5. F. BENGEL, *ibid.*, 1915, **29**, 247.
6. A. P. SCHULZ and G. S. STEINHOFF, *Zeit. Spiritusind.*, 1932, **55**, 162.
7. W. H. SYMONS, *Pharm. J.*, 1882, **13**, 237.
8. K. BAUMANN, *Zeit. Nahr. Genussm.*, 1899, **2**, 27.
9. G. EMBREY, *Analyst*, 1900, **25**, 315.
10. W. LENZ, *Zeit. öffentl. Chem.*, 1910, **15**, 224.
11. K. V. GIRI and P. N. BHARGAVA, *J. Indian Inst., Sci.*, 1936, **19A**, 53; K. V. GIRI, *Science*, 1935, **81**, 343.
12. W. HARRISON, *J. Soc. Dyers and Col.*, 1916, **32**, 40.
13. O. A. SJOSTROM, *Ind. Eng. Chem.*, 1936, **28**, 72.
14. O. SAARE, *Zeit. Spiritusind.*, 1884, **7**, 550.
15. H. S. McTAGART, *Can. Chem. Met.*, 1934, **18**, 8.
16. T. ZEREWITINOFF, *Zeit. anal. Chem.*, 1911, **50**, 680.
17. J. F. HOFFMANN and J. H. SCHULZE, *Woch. Brauerei*, 1903, **20**, 217.
18. S. MAQUENNE, *Compt. rend.*, 1905, **141**, 609.
19. H. TRYLLER, *Chem. Zeit.*, 1920, **44**, 833.
20. T. C. TAYLOR and J. M. NELSON, *J. Amer. Chem. Soc.*, 1920, **42**, 1726.
21. T. C. TAYLOR and L. LEHRMAN, *ibid.*, 1926, **48**, 1739.
22. H. TRYLLER, *Zeit. Spiritusind.*, 1934, **57**, 19.
23. W. F. A. ERMEN, *J. Soc. Chem. Ind.*, 1907, **26**, 501.
24. G. SCHUTZ and L. WEIN, *Chem. Zeit.*, 1915, **39**, 143.
25. G. BRUCKNOR and B. THOMAS, *Zeit. Getreid. Mühl. Bäcker.*, 1939, **25**, 34.
26. J. G. A. GRIFFITHS, *Analyst*, 1937, **62**, 510.
27. SPROCKHOFF, *Zeit. Spiritusind.*, 1929, **52**, 27.
28. T. H. FAIRBROTHER and R. J. WOOD, *Ind. Chem.*, 1930, **6**, 442.
29. BURTON and PITT, *Can. J. Res.*, **1**, 2, 155.
30. J. MAYRHOFER, *Oesterr. Chem. Ztg.*, 1935, **38**, 178.
31. C. SCHÉELE, J. AFZELIUS and K. LEANDER, *Zeit. Spiritusind.*, 1937, **60**, 163.
32. W. EKHARD, *ibid.*, 1929, **52**, 70.
33. SPROCKHOFF, *ibid.*, 1929, **52**, 358.
34. — *ibid.*, 1929, **52**, 341; *Chem.-Ztg.*, 1930, **54**, 411.
35. SCHULZ and PARLOW, *ibid.*, 1930, **53**, 135, 186.
36. E. T. REICHAERT, 'The Differentiation and Specificity of Starches in Relation to Genera, Species, etc.,' *Carnegie Inst. Publ.* **173**, 1913.
37. S. WOODRUFF and others, *Ind. Eng. Chem.*, 1938, **30**, 1409; *J. Agr. Res.*, 1936, **52**, 233; *Univ. Illinois Agr. Exp. Sta. Bull.*, **445**, 1938; *J. Agr. Res.*, 1933, **46**, 1108.
38. T. C. TAYLOR and SALZMANN, *J. Amer. Chem. Soc.*, 1933, **55**, 264.
39. T. C. TAYLOR, H. H. FLETCHER and M. H. ADAMS, *Ind. Eng. Chem. (Anal. Ed.)*, 1935, **7**, 321.
40. T. C. TAYLOR and J. C. KERESZTESY, *Ind. Eng. Chem.*, 1936, **28**, 502.
41. WIEDMER, *T.I.B.A.*, 1936, **14**, 103, 167.
42. O. SAARE, *Zeit. Spiritusind.*, 1903, **26**, 436; *Chem.-Ztg.*, 1929, **53**, 975.
43. E. VOGT, *Zeit. Unters. Nahr.-Genussm.*, 1921, **42**, 145.
44. T. E. WALLIS, *Pharm. J.*, 1922, **109**, 82.
45. W. A. RICHARDSON, HIGGINBOTHAM and FARROW, *J. Text. Inst.*, 1936, **27**, 131T.
46. W. A. RICHARDSON, *Chem. and Ind.*, 1939, **58**, 468.
47. HIGGINBOTHAM and W. A. RICHARDSON, *J. Soc. Chem. Ind.*, 1938, **57**, 234.
48. M. SAMEC and B. SKERL, *Kolloidchem. Beih.*, 1937, **47**, 91.
49. N. I. OZOLIN, *Trudy Odesskogo Inst. Tekhnol. Zerna i. muki im. I.V. Stalina* 1938, **81**.
50. C. SCHWEIZER, *Mitt. Geb. Lebensm. Hyg.*, 1925, **16**, 95; 1929, **20**, 119.
51. H. KÜHL, *Zeit. ges. Getreiden.*, 1930, **17**, 122; *Chem. Zentr.*, 1930, **11**, 1299.

52. E. BERLINER, *Mühlenlab.*, 1939, **9**, 13 and 87.
53. A. BINTZ and T. MARX, *Chemische Ind.*, 1909, **32**, 167.
54. H. CAPPENBERG, *Chem.-Ztg.*, 1910, **34**, 218.
55. V. VILIKOVSKI, *Chem. listy*, 1911, **5**, 412.
56. O. HOYER, *Chem. Zentralbl.*, 1911, **2**, 305.
57. W. NEUWOHNER, *Zeit. Tierernähr. Futtermitt.*, 1939, **3**, 1.
58. KLAUSS, *Vorratspflege Lebensmitt.*, 1938, **1**, Nos. 6 and 7.
59. M. I. KNYAGINICHEV, *Colloid J. (U.S.S.R.)*, 1939, **5**, 899.
60. T. J. SCHOCH and C. C. JENSEN, *Ind. Eng. Chem. (Anal. Ed.)*, 1940, **12**, 531.
61. F. ROBERTSON-DODD, *Analyst*, 1939, **64**, 735.
62. — *ibid.*, 1939, **64**, 877.
63. KAVCIC, *Koll. Beih.*, 1930, **30**, 406.
64. WINTON and WINTON, 'The Structure and Composition of Foods,' Vol. II. Chapman & Hall, London, 1935.
65. I. A. VESELOVSKII, *Amer. Potato J.*, 1940, **17**, 330.
66. C. R. JONES, *Cereal Chem.*, 1940, **17**, 135.
67. G. STEINHOFF, *Zeit. Unters. Lebens.*, 1938, **75**, 39.
68. J. KÖNIG and F. BARTSCHAT, *Zeit. Unter. Nahr. Genussm.*, 1923, **46**, 321 ; Abstr. in *Analyst*, 1924, **49**, 187.
69. R. STROHECKER, *ibid.*, 1924, **47**, 90 ; Abstr. in *Analyst*, 1924, **49**, 282.
70. M. WAGENAAR, *Zeit. Unters. Lebensm.*, 1937, **54**, 357.
71. L. PICKENS and D. T. ENGLIS, *Food Res.*, 1940, **5**, 563.
72. N. P. BADENHUIZEN and J. R. KATZ, *Z. physik. Chem.*, 1938, **182**, 73.
73. N. P. BADENHUIZEN, *Rec. trav. bot. néerl.*, 1938, **35**, 559.
74. R. W. KERR, 'Chemistry and Industry of Starch,' Academic Press Inc. N.Y., 1944.
75. J. R. FURLONG, *Chem. Trade J.*, 1943, 165 ; *Bull. Imp. Inst.*, Oct.-Dec. 1943.
76. F. D. ARMITAGE, *Industrial Chemist*, 1943, **19**, 61, 136, 267, 335, 383.
77. F. D. ARMITAGE, *ibid.*, 1943, **18**, 583.
78. RES. ASSOC. BRIT. FLOUR MILLERS, *Analyst*, 1943, **68**, 180.
79. W. VÖLKSEN, *Vorratspf. Lebensm.*, 1941, **4**, 270 ; *Chem. Zentr.*, 1942, **1**, 2466.
80. L. SAIR, *Ind. Eng. Chem., Anal.*, 1942, **14**, 843.
81. H. G. GREENISH, 'The Microscopical Examination of Foods and Drugs.'
82. L. H. ELIZER, *Ind. Eng. Chem. Anal.*, 1942, **14**, 635.
83. E. K. GLADDING and C. B. PURVES, *Paper Trade J.*, 1943, **116**, TAPPI, 150.
84. F. F. FARLEY and R. M. HIXON, *Ind. Eng. Chem. Anal.*, 1941, **13**, 616.
85. H. C. GORE and H. K. STEELE, *ibid.*, 1935, **7**, 324.
86. HAGEDORN and B. N. JENSEN, *Biochem. Z.*, 1923, **135**, 46.
87. MARTIN and J. N. NEWTON, *Cereal Chem.*, 1938, **15**, 456.
88. HASSID, *Ind. Eng. Chem. Anal.*, 1936, **8**, 138 ; 1937, **9**, 228 ; 1940, **12**, 142.
89. W. L. PORTER and C. O. WILLITS, *J. Assoc. Off. Agric. Chem.*, 1944, **27**, 179.
90. R. L. WHISTLER and G. E. HILBERT, *J. Amer. Chem. Soc.*, 1944, **66**, 1721.
91. K. A. CLENDENNING and D. E. WRIGHT, *Canad. J. Res.*, 1945, **23**, B, 131.
92. A. L. SHEWFEELT and G. A. ADAMS, *Can. Chem. Process Ind.*, 1944, **28**, 502.
93. A. R. LING, *J. Inst. Brewing*, 1922, **28**, 843.
94. R. M. SANDSTEDT *et al.*, *Cereal Chem.*, 1939, **16**, 780.
95. L. EYNON and J. H. LANE, 'Starch,' W. Heffer & Sons, Ltd., Cambridge, 1928.
96. *Bull. Imp. Inst.*, 1912, **10**, 566.
97. S. MUKHERJEE and S. BHATTACHARYYA, *J. Indian Chem. Soc., Ind. and News Ed.*, 1945, **8**, 4.
98. J. C. BAKER, H. K. PARKER and M. D. MIZE, *Cereal Chem.*, 1943, **20**, 267.
99. S. SCHMIDT-NIELSON and L. HAMMER, *Kgl. Norske Videnskab. Selskab., Forh.*, 1932, **5**, 84.
100. E. E. HUGHES and S. F. ACREE, *Ind. Eng. Chem. (Anal.)*, 1934, **6**, 123.
101. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 'Official and tentative methods of analysis,' 5th edit., A.O.A.C. Washington, D.C., 1941.

102. F. L. BATES, D. FRENCH and R. E. RUNDLE, *J. Amer. Chem. Soc.*, 1943, **65**, 142.
103. R. W. KERR and G. SEVERSON, Paper to Div. Agr. Food Chem. Sugar Chem. Tech., Amer. Chem. Soc. Meeting, 1942, April 23rd.
104. R. W. KERR and O. TRUBEL, *Cereal Chem.*, 1941, **18**, 530.
105. K. H. MEYER, P. BERNFELD and J. PRESS, *Helv. Chem. Acta*, 1940, **23**, 865.
106. T. E. WALLIS, *Pharm. J.*, 1919, **103**, 75.
107. — *Analytical Microscopy*, 1923.
108. M. NYMAN, *Z. unters. Nehr. u. Genussm.*, 1912, **24**, 673.
109. M. M. TAHA EL-KATIB, *Analyst*, 1946, **71**, 559.
110. K. NEHRING and J. SCHÜTTE, *Vorratspflege u. Lebensm.*, 1942, **5**, 398.

ADDITIONAL REFERENCES

- F. PUGH, *Microscope*, 1938, **2**, 239. (Qualitative and quantitative microscopical examination of starches.)
GASTINE, *Compt. rend.*, 1906, **142**, 1207; *J. Soc. Chem. Ind.*, 1906, **25**, 655. (Detection of rice flour in wheat flour.)
W. N. JONES, *Ann. Bot. (N.S.)*, 1939, **3**, 505. (Preparation of double stained slides of starch and plastids.)
L. ROSENTHALER, *Pharm. Zentr.*, 1925, **66**, 631. (Starches heated with alcoholic caustic potash, diluted with waters, titrated give characteristic numbers.)
W. KRÖNER, *Zeit. ges. Getreidew.*, 1939, **26**, 162. (Colour, odour, gloss, moisture, ash, acidity, etc., of potato starch discussed.)
C. H. BUTCHERS, *Food*, 1934, **3**, 244. (Microscopy of starch discussed.)
S. CAMILLA, *Ann. Chim. Applic.*, 1938, **28**, 541. (Characteristics of starch granules originating in the dried bulb in powdered saffron described.)
C. GRIEBEL, *Z. Unters. Lebensm.*, 1927, **54**, 477. (Notes some hazel nuts contain starch contrary to previous assumptions that they do not.)
J. H. VAN DE KAMER and N. F. JANSEN, *Analyt. chim. Acta*, 1949, **3**, 397. (Determination of water using phosphorus pentoxide in vacuum.)
O. FERNANDEZ and R. O. MAZÓN, *Farm. nueva* (Madrid), 1944, **9**, 625. (Analytical figures for starches from *Oxalis violacea* (L), *Cyperus esculentus* (L), *C. rotundis* (L), and *Aesculentus hippocastanum* (L).)
J. E. CLELAND, E. E. FAUSER and W. R. FETZER, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 334. (Tables showing Baumé values, specific gravity and dry substance contents of maize starch suspensions.)
D. M. BATSON and J. T. HOGAN, *Analyt. Chem.*, 1949, **21**, 718. (Estimation of water in sweet-potato starch by specific gravity method.)
B. LAMPE, *Z. Spiritusind.*, 1930, **52**, 357. (Determination of starch in potatoes by weighing in air and water.)
C. GRIEBEL, *Z. Lebensm. Unters. u-Forsch.*, 1948, **88**, 269. (New and unusual forms of pea starch found in peas and pea flour from 1947 crop described.)

CHAPTER 17

THE DETERMINATION OF STARCH

MANY methods are in use for the determination of starch, but most of them are applicable to a limited type of work only. They may be roughly classified under the following headings :—

1. Non-hydrolytic Methods.—In these the starch is dispersed in a solvent, and then (*a*) recovered and weighed, or (*b*) precipitated from the solvent in the form of a derivative, or (*c*) determined polarimetrically.

2. Hydrolytic Methods.—In these the starch is hydrolysed to reducing sugar and the sugar determined. The inversion may be carried out by means of (*a*) acid, (*b*) enzymes, or (*c*) enzymes, followed by acid treatment.

Non-hydrolytic Methods (*a*).—Various acids, such as hydrochloric and trichloroacetic,² salts such as calcium chloride,^{35, 116} potassium thiocyanate, zinc chloride,¹ and magnesium chloride⁸², caustic alkalis, glycerol and formamide have all been used to disperse starch, which can then be recovered without undergoing appreciable hydrolysis, although its physical properties may have been radically altered.

One of the most reliable methods is that of O. Rask,³ which has been tentatively adopted in America by the Association of Official Agricultural Chemists.⁴ The starch is dispersed in cold concentrated hydrochloric acid to give a filterable solution from which the starch is recovered by precipitation with alcohol. The recovered starch has lost its identity, as seen under the microscope, and is water-soluble, but still gives the iodine reaction, and does not reduce Fehling's solution, but A. R. Ling and F. E. Salt⁵ consider that some hydrolysis occurs. C. W. Herd and D. W. Kent-Jones⁶ do not think that the method is entirely satisfactory, and to overcome its defects have modified it, reducing the manipulative difficulties to a minimum when dealing with flours, wheats, brans, sharps, and all classes of mill stocks. One gram of the material is well mixed with 1 gm. of acid-washed sand and covered with ethyl ether in a centrifuge tube, well stirred for about 1 minute, after which it is centrifuged and the liquid poured off. This is repeated twice more, so reducing the filtration difficulties, due to impurities, which would arise later in the

determination. To the residue is added 2.5 ml. water and 0.25 ml. N/1 caustic soda solution, which is thoroughly stirred in. Fifteen minutes later 5 ml. of pure methyl alcohol are added and mixed in, followed by 5 ml. of dilute methyl alcohol (5 ml. alcohol, 2.5 ml. water), and after mixing and centrifuging the alcoholic layer is removed. The residue is washed twice with 10 ml. of the diluted alcohol, and finally given three washings with water.

The residue is mixed to a thick paste with a few ml. of water, taking care that no lumps are formed. A total of 20 ml. of water is employed to transfer the paste to a 100 ml. flask, to which 20 ml. of concentrated hydrochloric acid are then added, and the total volume is made up to 100 ml. with Rask's acid, using this first to rinse out the centrifuge tube. After shaking the flask, the contents are filtered through a Gooch crucible having a layer of acid-washed sand superimposed on the asbestos; 50 ml. of the filtrate are pipetted into a 200 ml. beaker containing 110-115 ml. of 96 per cent. alcohol, and not until the pipette has drained is the liquid in the beaker thoroughly stirred. A flocculent precipitate is formed; after it has partially settled the contents of the beaker are centrifuged for 10 minutes and the residue washed four times with 70 per cent. (by volume) alcohol and twice with 96 per cent. alcohol to remove the last trace of acid, care being taken that the residue and alcohol are thoroughly mixed each time.

It is essential that the time between the addition of the acid to the sample and the precipitation of the starch with the alcohol does not exceed 35 minutes, otherwise hydrolysis of the starch may materially affect the results. The final residue is transferred to a tared Gooch crucible, using 96 per cent. alcohol, washed with ethyl ether and dried in the oven at 40° C. for 10 to 15 minutes; this is followed by heating to 130° C. until the weight is constant.

For 'sharps' or bran, these workers recommend starting with 2-4 gm. of material, increasing the methyl alcohol and caustic soda mixture in proportion, and retaining the crude fibre on glass before making up the volume to 100 ml.

With commercial starches the above method was found to give results nearer to 100 per cent. than methods using malt or barley diastase, but the results on commercial flours and wheat offals were lower.

L. Jones⁷ and O. S. Rask⁸ find that variations occur between the figures obtained by Rask's method and those obtained by diastatic methods. F. E. Denny⁹ suggests that the material be gelatinised with water, extracted with four successive portions of

acids, precipitating the starch in these with alcohol, and then acting on the starch present with takadiastase (see below). In this way he proposes to overcome the incomplete extraction of starch by the above method and at the same time eliminate the inclusion of non-starch fractions in the alcoholic precipitate.

M. P. Etheridge¹²³ has compared the results using Rask's method with those obtained by Hopkins' modification of the Mannich-Lenz polarimetric method and finds the former gives somewhat lower results on bread, Argo starch, corn meal and rice puffs but slightly higher results with flour. The use of sulphosalicylic acid instead of calcium chloride as the dispersing agent in the Hopkins method gave low and inconsistent results, acetic acid gave low results but seemed to offer possibilities. It is of interest to note that this worker tried the following compounds as dispersing agents but without success:—Chloramine T, sodium-phenate, resorcinol, ammonium acetate, diphenyl ether, sulphonal, p nitro-phenol, 2·5 dinitrobenzoic acid, thiourea and several alcohols.

In further work this worker¹²⁴ finds the Rask method inapplicable to baked cereals and considers the Hopkins polarimetric method or the diastase-hydrochloric acid method¹²⁵ offer better alternative possibilities. With sweet potato starch the results on a dry weight basis with Hopkins' method were over 100 per cent. indicating that $[\alpha]_D = 200$ for wheat starch is not satisfactory for other starches and that it may be necessary to determine the $[\alpha]_D$ for each starch before this method could be used (see p. 363). The diastase-hydrochloric-acid method appears to be more generally applicable, although in the case of starch in sweet potato both methods erred to a similar degree. In a further paper¹³⁶ he concludes that the Hopkins (Mannich-Lenz) polarimetric method is as good as, if not better than, any other known method. He considers calcium chloride is not an ideal dispersion medium and the glucose factor of 0·9 is too low.

W. H. Krug and H. W. Wiley¹⁰ use salicylic or lactic acid under pressure to disperse the starch, but their method gives high results due to the degradation of pentosans and hemicelluloses, whilst P. Biourge² uses a 3 per cent. solution of trichloroacetic acid.

Other workers have used alkali to disperse the starch, for example, J. Mayrhofer¹¹ and M. Piettre¹² treat foodstuffs with alcoholic caustic potash, which dissolves fats, sugars, and albumins. After filtering, the residue is treated with aqueous caustic potash, the solution acidified, and the starch precipitated with alcohol, washed and dried. G. Baumert and H. Bode¹³⁻¹⁴ use caustic

soda to dissolve the starch, precipitate it with alcohol, dissolve the precipitate in hydrochloric acid and re-precipitate with alcohol, after which the dried residue is ignited and the loss on ignition is taken as the weight of starch present. P. Behrend and H. Wolfs¹⁵ state that this method gives accurate results.

Non-hydrolytic Methods (b).—The formation of additive products between starch and iodine was used by A. Kaiser¹⁶ as a method for determining starch, and later Th. von Fellenberg^{17,18} used calcium chloride solution to dissolve starch, which was then precipitated by the addition of iodine solution. The calcium chloride acts as a salting-out agent for the starch-iodine complex, and this is decomposed with alcohol to give starch. J. J. Chinoy and F. W. Edwards,¹⁹ other workers,^{20,21} and H. Weiss²² have used similar methods. J. C. Small²³ uses ammonium sulphate to salt out the starch iodide from aqueous dispersions and to remove the dextrin-iodine complexes present. W. Whale,⁶⁸ using an iodometric method for food products, points out that the presence of dextrin introduces an error not easily overcome, and in such cases advocates one or other of the hydrolytic methods. He has successfully applied the volumetric iodide method to the determination of starch in cocoa and sweetened chocolate.⁸⁰

F. E. Denny^{24,25} determined the amount of starch, first by precipitation with iodine, which was then titrated, and later by hydrolysing the starch to glucose by means of takadiastase. J. T. Sullivan²⁶ has applied the method to the estimation of starch in woody plants, and hydrolyses the starch-iodide precipitate to glucose with acid. Although his results are lower than those obtained by other methods, he considers them to be accurate. Tian²⁷ has attempted to eliminate errors due to the indefinite composition of starch iodide. Using dilute aqueous solutions of starch, an excess of iodide solution is added and the colour matched against standards, red light being used for the comparisons, as this light is absorbed only by the starch iodide and not by the excess iodide present (see also Vol. I).

P. Biourge² dissolves the starch in 3 per cent. trichloroacetic acid, and after adding iodine solution, the starch-iodine complex is salted out with magnesium sulphate. G. Rankoff⁸⁴ determines starch in potato meal by extracting it with calcium chloride, precipitating with I/KI solution saturated with sodium sulphate, washing, heating with 25 per cent. sulphuric acid to remove iodine and determining the starch by oxidation with potassium permanganate.

A. von Asboth²⁸ has suggested a method based on the forma-

tion of a sparingly soluble barium salt of starch, but other workers consider the method unreliable.²⁹

Non-hydrolytic Methods (c). Solvents Used.—In the third class of non-hydrolytic methods the starch is dispersed or dissolved in a solvent and the amount of starch present in solution is determined by means of the polarimeter. Methods depending on the use of this instrument presuppose a constant specific rotation value for the starches occurring in definable classes of plant materials. Unfortunately there appears in the literature values for the specific rotation of starch ranging from -180° and $+220^\circ$. To quote French¹³¹ '... one is tempted to believe that each worker has his own method...'. A number of agents have been used to prepare the starch solutions for polarimetric measurement. A. Baudry^{30,31} refluxes the sample with benzoic or salicylic acid and examines the filtrate polarimetrically, the polarimeter being graduated for reading the starch-content directly. A modification of this method has been used by L. Pellet.³² Effront³³ uses hydrochloric acid as the solubilising agent, and after polarisation makes allowance for the small amount of glucose present, which he determines by titrating with Fehling's solution. D. Crispo³⁴ uses caustic potash solution for polarising, and C. Mannich and K. Lenz³⁵ boil the starch with a concentrated solution of calcium chloride, which is N/500 with respect to acetic acid, and thus obtain a clear solution suitable for direct polarimetric observation. Calcium chloride solutions are also favoured by Hopkins.¹³⁴

The Mannich-Lenz procedure or its modifications have been favoured by a number of workers (see Table 10), but K. A. Clendenning¹²⁹ finds it unsuitable for the determination of starch in gluten and describes an improved method. The sample is boiled for 15 minutes with a calcium chloride solution (d 1.30) of approximately pH 2.5. Frothing is controlled by the addition of one or two drops of *n*-octyl alcohol, constant volume being maintained during boiling by the addition of water. The dissolved proteins are precipitated with 20 per cent. stannic chloride solution prior to filtration and polarisation. The procedure is rapid and the starch found is low but a correction can be made so that the final, corrected figure for starch is within ± 0.5 per cent. of the true value.

Earle and Milner¹³⁰ have determined the specific rotation of maize (2), wheat (2), waxy maize, tapioca and potato starches, using calcium chloride dispersions in an improved polarimetric method. The specific rotations were 203.5, 202.6, 202.4, 201.2, 203.8, 203.5 and 203.7, respectively. These results were in

close agreement with those obtained by the diastase-acid hydrolysis method with a conversion factor of 0.92 instead of 0.9. The method was also applied to rye, barley and sorghums. The calcium chloride method appears to be one of the most consistent and is discussed more fully below.

Methods Based on Hydrochloric Acid Solutions.—C. J. Lintner^{36, 135} triturates 5 gm. of the sample with 20 ml. water, then mixed with 40 ml. concentrated hydrochloric acid, and after standing 30 minutes transfers to a flask, using hydrochloric acid of sp. gr. 1.125. Ten ml. of a 4 per cent. phosphotungstic acid solution are added and the volume made up to 200 ml. with hydrochloric acid (sp. gr. 1.125). After filtering the solution, the rotation is determined in a 200 mm. tube with sodium light. Lintner found $[a]_D^{20} = 200.3$ for barley starch. The amount of starch in a sample can be found from the formula

$$\text{Percentage} = \frac{4,000 \times \text{observed rotation}}{L \times [a]_D^{20}}$$

where L = length of tube in decimetres and $[a]_D$ = specific rotatory power of barley starch under above conditions.

O. Wenglein³⁷ used sulphuric acid instead of hydrochloric acid and obtained for barley starch a specific rotatory power $[a]_D = 191.7$. Lintner^{38, 39} has also used this method, but thinks that the sulphuric acid used by Wenglein may cause decomposition of the starch and suggests using a weaker acid of sp. gr. 1.4.

Although M. Canet and O. Durieux⁴⁰ found Lintner's method to be satisfactory with starch and amylaceous materials, they suggest the specific rotatory power $[a]_D^{20} = 202$ be used in the above formula. The specific rotatory powers of the more important starches have been determined by J. König and co-workers,⁴¹ using Lintner's hydrochloric acid method and Ewers' method (see below). Their results show that the starch probably undergoes hydrolysis during the precipitation of the solution by Ewers' procedure, and that noticeable errors would be introduced into the determination by this method if the average value of $[a]_D^{20}$ was taken, as the rotations for different starches vary more widely than by Lintner's method. With the latter method, the value $[a]_D^{20} = 202$ is sufficiently accurate for ordinary work. The two methods have also been compared by S. Hals and S. Heggenhangen.⁴²

E. Ewers⁴³ treated the starch with glacial acetic acid, hydrochloric acid and hot water, and used potassium ferrocyanide to

clear the solution, allowance being made for the rotation due to soluble carbohydrates. Later⁴⁴⁻⁴⁶ he used dilute hydrochloric acid (1·124 per cent. by weight) with which the starch was heated, clarified with sodium molybdate or phosphotungstic acid, filtered and polarised. The details of Ewers' method are as follows:— 5 grams of finely powdered material are washed into a 100 ml. graduated flask with 25 ml. of 1·124 per cent. hydrochloric acid, a further quantity of the same acid being used to wash down the neck of the flask after it has been thoroughly shaken with the first acid addition. After several more shakings the flask is heated in a boiling water bath for exactly 15 minutes, during the first three of which it is constantly rotated. After making up, with cold water, to about 90 ml. 2 ml. of sodium molybdate solution, made by fusing 30 gm. of molybdic acid with 25 gm. dry sodium carbonate and dissolving the product in water, making up to 250 ml. and filtering. Alternatively, 10 ml. of a 4 per cent. solution of phosphotungstic acid may be added, the volume made up to the mark with water, the flask shaken, the liquid then filtered and polarised in a 200 mm. tube. If a saccharimeter is used, the percentage of starch is obtained by multiplying the Ventske reading by 1·912. The specific rotation for barley starch was found to be 181·5 by this method. A similar method was employed by him for estimating starch in potatoes.⁴⁵ V. Jahn,⁸³ estimates the amount of starch in sausages, meat pastes or mayonnaise by applying Ewers' method to the residue from extraction with alcoholic potash in the following manner: 20 gm. of the material are digested for several hours on the water-bath with 50 ml. of 8 per cent. alcoholic potash, and, after filtering, the residue is washed with 96 per cent. alcohol, water being added to make a total weight of 25 gm. The mixture is treated with 0·5 N hydrochloric acid until neutral to phenolphthalein, after which it is heated with 25 ml. dilute hydrochloric acid (80 ml. of 25 per cent. acid diluted to 1 litre) at 100° C. for 15 min. to disperse the starch. After cooling 6 ml. of a 4 per cent. phosphotungstic acid solution are added, the whole diluted to 100 ml., clarified with kieselguhr, and filtered. The filtrate is examined in the polarimeter and the reading on the sugar scale $\times 0\cdot475$ represents the percentage of pure starch present. M. I. Knyaginichev and Y. K. Palilova⁸⁵ have found that starch from legumes have a lower specific rotation ($[a]_D^{20} = 192\cdot7$) than that from wheat starch, and consider that the value of the specific rotation runs parallel with the degree of evolutionary development. They found, for example, that the starch from primitive varieties of scaly grain wheat has a lower specific rotation ($[a]_D^{20} = 199\cdot8$)

than that from cultivated varieties with naked grain ($[a]_D^{20} = 204 \cdot 0$). The significance of this in botanical and horticultural investigation will be appreciated. J. Kavčič⁸⁶ has also found that the starch from four different varieties of *Solanum tuberosum* (potato) showed different values for optical rotation as well as for mean diameter of grains, ash, and nine other different properties of the starches. The values of these properties were consistent within any one variety but differed from the corresponding values for other varieties.

Table XXIII shows the figures obtained by J. König and co-workers¹²⁰ using both Ewers' and Lintner's methods on the same starches. Ewers' method gives considerably lower rotations and vary much more with different starches. A mean value could not be used for all without serious error in some cases. The percentages of starch were obtained both by difference, i.e. 100 minus the sum of the percentages of other constituents and by hydrolysis to dextrose and estimation of the sugar which is considered the more accurate method of the two.¹²¹

TABLE XXIII

Starch.	$[a]_D$ Lintner Starch by		$[a]_D$ Ewers Starch by	
	Difference.	Hydrolysis.	Difference.	Hydrolysis.
Potato .	201·2	204·5	191·8	195·0
Maize .	201·2	205·2	182·5	186·2
Rice .	200·8	203·2	185·8	188·0
Wheat .	200·3	203·8	182·7	185·9
Rye .	200·4	205·8	—	182·9
Barley .	198·2	205·5	180·0	186·7
Oat .	193·2	201·8	—	180·0
Millet .	183·7	201·2	—	165·5
Bean .	204·6	208·3	169·4	172·4
Lentil .	195·8	204·8	181·3	185·4
Pea .	198·0	201·0	185·0	187·8
Buckwheat	199·6	201·6	170·0	171·7
Arrowroot	198·6	201·9	182·9	185·0
Maranta .	204·7	212·7	177·4	184·3
Palm sago	202·6	209·6	180·3	186·5
Cassava .	203·9	210·9	181·5	187·7
Pepper .	201·9	207·8	179·2	184·5
Banana ¹²²	209·8	—	196·4	—

When examining substances containing optically active constituents in addition to the starch, resort can be made to thorough washing with cold water, alcohol and ether, to remove the interfering substances,

Thus it will be seen that there are widely different values obtained for the specific rotation of starch and in the literature values ranging between $[\alpha]_D = +180^\circ$ and 220° may be found. This may arise partly from the difficulty of obtaining clear and undegraded solutions of starch, for most values reported for high molecular weight dextrans which are readily soluble lie in the much shorter range of $[\alpha]_D = +190^\circ$ and 200° . Meyer dissolved 'amylose' in alkali, neutralised and measured the optical rotation immediately and obtained a value of $[\alpha]_D = 220^\circ \mp 5^\circ$.¹³² This value is much higher than the generally accepted values for whole starch. Aqueous solutions of amylopectin are highly opalescent and somewhat opaque and give a somewhat uncertain value of $[\alpha]_D = +200^\circ$. Kerr reports¹³¹ that freshly prepared amylose, butanol precipitated, gives clear solutions giving $[\alpha]_D = 200^\circ$ with an uncertainty of about 2° . With this material there is usually a small amount which is undissolved even after several minutes boiling and furthermore it contains butanol and water of hydration so that solutions of known amylose strength are not easy to prepare. The amount of amylose in solution, however, can be determined by evaporating an aliquot portion of the liquor, used in the determination, to dryness.

Freudenberg's equation¹³³

$$[M]_n \neq [M]_2 + (n-2) [M]_{\infty/\infty}$$

(where n is the number of glucose residues in the amylose chain $[M]_n$ and $[M]_2$ the molecular rotations of an n -membered amylose chain and maltose, respectively, and $[M]_{\infty/\infty}$ is the molecular rotation per glucose unit of an infinitely long amylose chain) allows one to calculate the value of the specific rotation of an amylose chain of any given number of glucose units after calculating that of an infinite chain of glucose residues. The fact that amyloextrins give clear solutions is of great value here, as, for example, with an amyloextrin of 22 glucose residues having a specific rotation of $[\alpha]_D = +193^\circ$, maltose with $[\alpha]_D = +131^\circ$ the respective molecular rotations are $[M]_{22} = 691,300$ and $[M]_2 = 47,200$. The molecular rotation per glucose residue is $[M]_{\infty/\infty} = 32,200$, which corresponds to a specific rotation for the infinitely long amylose chain of $+199^\circ$, agreeing quite well with the figure obtained with butanol-precipitated amylose.

Methods Employing Calcium Chloride Solution.—Ether-edge¹³⁶ has found that the starch content that is reported by different workers varies widely when the Mannich-Lenz-Hopkins procedure is applied to equal weights of the same sample of starch; for a single sample of maize starch the various workers

reported starch contents ranging from 85.74 per cent. to 90.88 per cent. while with wheat starch the variation was from 85.75 per cent. to 89.45 per cent. It has been reported¹³⁷ that starch concentration has an important effect on the specific rotation value, causing it to decrease from $+207^\circ$ at 0.9 per cent. to $+199.4^\circ$ at 5.6 per cent. starch under the conditions of the Lintner method. Mannich and Lenz presented data upon the effect of various factors upon the optical rotatory power but their work was confined to wheat starch and they did not indicate how they determined the 'true starch content'. The multiplicity of optical rotatory values for starch and of the methods and conditions for obtaining these values constituted a most unsatisfactory state of affairs. Fortunately K. A. Clendenning and D. E. Wright¹³⁸ have now investigated the effect of solvent, pH , salt concentration, extraction temperature and time, filtration technique, starch concentration and polarisation temperature upon the optical rotatory power of wheat starch dissolved in aqueous calcium chloride solutions. Clendenning¹³⁹ then extended this work to other starches. He found that the addition of small amounts of 0.8 per cent. acetic acid to concentrated calcium chloride solutions as practised in the Mannich-Lenz method causes a remarkable increase in the pH value. With 15 minutes boiling at pH 2.1 to 3.0 little effect was exercised on the specific rotatory power; above pH 4.0 the starch solutions are cloudy, difficult to filter and gel on standing; at pH values below 2.0 the specific rotatory power is depressed. The specific rotatory power is depressed by rising extraction temperature to an extent varying with time and pH value but is unaffected up to 1 hour boiling period between pH values of 2.2-2.5. It is increased quite remarkably, however, by rising salt concentration. Substituting magnesium chloride for calcium chloride increased the specific rotation value for wheat starch approximately 7° . The concentration of starch appears to have a negligible effect but a rising polarisation temperature causes a decrease in the value over the temperature range of 20° C. to 35° C.

Clendenning considers a satisfactory solution of calcium chloride to be one having a density of 1.30 adjusted to pH 2.2-2.5 by the addition of 2 c.c. of 0.8 per cent. acetic acid to 60 c.c. of the essentially unadjusted salt solution (pH 5.5), or by acidifying the salt solutions *en masse* with glacial acetic acid as suggested by Earle and Milner.¹³⁰ At this acidity level the specific rotatory value is relatively insensitive to variations in the time of heating provided alterations in salt concentration are avoided. A suitable boiling time appears to be about 15 minutes. After heating

the solution is cooled and the volume adjusted with distilled water. With starches of low fat content no cloudiness is occasioned by this step. The specific rotation is depressed, however, because of the accompanying decrease in salt concentration.¹⁴⁰ Clendenning prefers to use calcium chloride solution of the same temperature. Filtration is generally required and the first fractions of filtrate should be discarded as otherwise the sorptive properties of the filter paper for water give high values.

The filtrate is transferred to water jacketed 2 dm. polarimeter tubes, the temperature being maintained constant since a relationship exists between the specific rotation value and polarisation temperature, the relationship being expressed tentatively by the expression $[\alpha]_D^t = [\alpha]_D^{20} - 0.12(t - 20)$. A similar relationship exists in the case of sugars.^{141, 142} Rotating the tube while viewing the field¹⁴³ reveals cover glasses rendered optically active, by pressure from the screw-caps, or eccentricity of the tube. Handling the tubes by the caps only is recommended by Browne and Zerban¹⁴² in order to avoid heating of the tubes by the hands thus leading to striations, which may also arise if the tube is insufficiently rinsed out with the solution before the final filling.

Clendenning and Wright have applied the above method to various samples of starch from the same species or genus, and from different varieties grown in different locations.

The specific rotation values for 48 samples of starch representing 20 different genera or species showed little divergence from 203° . Hard, soft and durum wheats gave starches having values lying between 202.3° to 203.2° . Average values for various starches were wheat, -202.7° ; maize, -202.9° ; waxy maize, -202.3° ; barley, 203.5° ; waxy barley, 202.5° ; rye, 202.8° ; oat, 202.9° ; rice, 203.0° ; waxy rice, 202.7° ; grain sorghum, 203.2° ; waxy sorghum, 202.3° ; buckwheat, 203.4° ; millet (impure), 201.4° ; sweet potato, 203.4° ; arrowroot, 203.3° ; tapioca, 202.8° ; potato, 204.1° ; lily (bulb), 203.9° ; pea, 199.4° ; bean, 200.2° ; and lima bean, 200.5° . If starch is stored for periods of time longer than ten years a decrease takes place in the specific rotation value. Thus the root, bulb and tuber starches show specific rotation values that, on the whole, corresponded closely with those of the cereal starches, potato starches having the highest values. The legume starches were characterised by low values averaging 200° . There were probably some impurities present, but in view of the care exercised by these workers in preparing these starches it appears advisable from the present evidence to employ

this lower value in analytical applications of the calcium chloride polarimetric procedure to legume products.

Thus a specific rotation value of $+203^\circ$ is suitable for calculations of starch content in most applications of the calcium chloride polarimetric procedure, although potato and legume starches have higher and lower values ($+204.2$, $+200^\circ$), respectively should be employed. It now appears that the specific rotation value of starch from the same genus does not vary widely with the conditions under which the starch is formed in the plant. Very old starch samples are unsuitable for standardisation purpose or for fundamental studies in this field since Clendenning and Wright found wheat starch 10 years old to give a specific rotation of $+199.8^\circ$ and one 18 years old a value of 197.6° .

R. T. Balch¹¹⁸ finds that by using sodium hypochlorite as a dispersing and solubilising agent filtration difficulties are overcome, and after filtration a clear liquid is obtained which can be examined in the polariscope without difficulty. The residue with root starches contains no starch, but with grain starches only 93-94 per cent. of starch is removed. Balch considers this may be due to the residue retaining the so-called amylohemiacellulose, stated to occur in grain but not root starches, which is convertible by the diastatic or acid hydrolysis methods, so that it is included in the determination of starch by the usual methods.

Hydrolytic Methods (a).—As previously stated, the amount of glucose obtained by acid hydrolysis of starch multiplied by the factor 0.90 should indicate the amount of starch present, but W. A. Noyes and co-workers⁴⁷ consider that a complete recovery cannot be obtained unless the factor 0.93 is used. This is a completely empirical figure, but it has been adopted by a number of workers, as losses certainly do occur which may be due to the presence in the hydrolysate of disaccharides having a lower reducing power than glucose. Once it has been formed, the glucose undergoes no change on heating with acid, unless the concentration of the latter is abnormally high or the duration of the heating is excessive.⁴⁸ Acid-hydrolysis methods are limited to starch determinations in materials which are free from other cellulosic materials which may also yield glucose on treatment with boiling acid. Cellulose is less readily attacked by dilute acid than starch at about 60-80° C. for a short time, and G. S. Fraps⁴⁹ uses 0.02 N acid to separate the starch from the insoluble matter, completing the hydrolysis with stronger acid in the usual way and correcting the results for the pentosans present.

Ling⁵⁰ considers that none of the polarimetric methods in which acid is used as a converting agent gives reliable results, at

any rate, for starch in cereals, because certain other substances pass into solution.

Hydrolytic Methods (b).—As the products of enzyme action on starch consist of a mixture of sugars and dextrans, numerous methods have been elaborated that embrace both enzymatic and chemical or physical treatments. Enzymatic methods are most useful where other carbohydrate material, capable of hydrolysis to glucose with acid, is present besides the starch.

Several methods of an empirical kind which yield products giving definite values for the reducing power or the rotation of polarised light must be carried out under strictly controlled conditions. In other methods the amount of each end-product present in the mixture is found by different ways, and the amount of each product present calculated by the use of simultaneous equations. A third group of methods comprises those in which a preliminary enzymic reaction is used to separate the starch from other bodies present; the separated degradation products are hydrolysed to glucose, which is estimated and the amount of starch deduced.

Barley and Malt Diastase Methods.—So many diastatic methods have been proposed and employed that only a few can be mentioned here.

Both α - and β -amylase are present in malt, the former causing liquefaction of the starch and the latter, the so-called saccharogenic enzyme, converting the amylose to maltose (see Vol. I). E. Waldeschmidt-Leitz, M. Reichel and A. Purr⁵¹ have shown that, contrary to previous belief, both enzymes are present in varying amounts in ungerminated barley, and G. Nordh and E. Ohlsson⁵² have found that both enzymes possess saccharogenic and dextrinogenic activity. Such observations throw doubt on the accuracy of the results obtained by the method of Ling, Nanji, and Harper,⁵³ in which the precipitated, undried diastase from ungerminated barley⁵⁴ is used on the assumption that only the amylose is attacked, and that the ratio of amylose to amylopectin is 2-1. As previously stated (see Vol. I), the accuracy of this ratio is disputed by several workers,⁵⁵⁻⁵⁷ although H. Lüers and F. Wieninger⁷⁴ found the method gives concordant results.

Simultaneously with the barley or wheat conversion, Ling and his co-workers make a blank estimation, using high-grade potato starch, and determine the amount of maltose present, either iodometrically or by Fehling's method, expressing the result as a percentage of the starch. The percentage of starch in the barley or wheat is expressed as $100m/M$, in which m is the maltose obtained from 100 pts. of dry cereal and M is the maltose present

in the potato-starch experiment expressed in 100 pts. of the dry starch. The accuracy of the method depends on the amylose-maltose figure for potato starch and the extent to which this is applicable to other starches and cereal products. If this relationship holds the method is reliable and precise.

In a number of methods germinated barley is used, and maltose, together with a small amount of dextrans of varying constitution, is produced. Ling⁵⁸ has used malts with a diastatic activity of 20-100, as measured by his scale, under strictly controlled conditions, and has obtained maltose corresponding to 80-87.5 per cent. of the weight of starch. In determining the amount of starch in cereal products the amount of maltose produced is compared with that theoretically obtainable by the same malt. Ling and Price^{75, 76} propose to avoid limiting the method to the use of malt of diastatic power of 80 Lintner by means of a simple formula.

H. T. Brown^{59, 60} extracts the malt or barley for 9 or 3 hours, respectively, with alcohol to remove sugars and certain nitrogenous compounds, boils the sample under examination with water, and digests it at 57° C. with an active malt extract. After 1 hour the liquid is boiled, cooled, and filtered, and the maltose-content determined. The starch equivalent to this maltose-content is calculated on the assumption that 84.4 pts. of maltose correspond to 100 pts. of starch. This assumption is justified only if the malt from which the active extract is prepared has a diastatic power of 80 Lintner, but malts with a lower diastatic activity give less, and highly active malts give more, maltose than the above figure. Considerable error has been found to occur when starch in sweet potatoes is estimated with the malt diastase method using the usual procedure. Pretreatment with calcium or barium hydroxide solution prevents, to a very great extent, the action of malt diastase on certain non-starchy constituents usually determined as starch, and for the most accurate determination of starch in sweet potatoes such pretreatment has been found to be essential.¹²⁷

C. F. Poe and B. P. Jukkola¹⁴⁴ have examined the effect of seven commonly used preservatives on the diastase method for determining starch. In most cases an increasing amount of preservative resulted in a lower starch recovery this effect being chemical rather than due to change in pH. The amount of the decrease in the percentage of starch recovered is not significant inasmuch as the amounts of the preservative used were far in excess of those ordinarily found in food products which are generally examined for starch. Potassium nitrate, boric acid and borax have little effect, sodium bisulphite or salicylate were detrimental

in amounts over certain limits, whilst sodium benzoate had the largest effect.

Takadiastase.—Takadiastase preparations, which contain many different enzymes,⁶¹ were introduced as a quantitative reagent for determining starch by W. A. Davis and A. J. Daish⁶² in 1914. I. D. Collins⁶³ pointed out that, at proper pH value and correct time, a high concentration of the enzyme gives complete hydrolysis to glucose, basing her conclusions on the fact that takadiastase, and also acid hydrolysis, gave a recovery of 93 per cent. of the dry weight of starch; if the factor 0.93 is used, she suggests that a recovery of nearly 100 per cent. is obtained. Denny²⁵ and O. Lehmann⁶⁴ report complete recovery of starch by this method. The use of takadiastase is widespread among workers on plant products, and thus deserves attention, but it should be remembered that these preparations also contain enzymes which act on materials other than starch, so that its use should be examined critically before trying any new unproven departure from previous work.

J. H. Van de Kamer¹²⁶ has suggested boiling the disintegrated, starch-bearing material with water and treating the extract with pancreatic amylase, after which the reaction mixture is centrifuged to remove pentosans and hemicelluloses and the sugars determined. Too many unknown and variable factors appear to enter into consideration in this method to warrant its use before it has received critical attention.

Hydrolytic Methods (c).—Methods embracing the acid hydrolysis of the products obtained by enzyme action have found wide favour in America. Maerker⁷⁰ extracts 3 gm. of the finely-ground material with ether, after which it is boiled with 100 ml. of water, cooled to 65° C. and treated for about 2 hours with 10 ml. of a 10 per cent. infusion of malt. It is then heated on a boiling water-bath for 30 minutes. On cooling to 65° C. another 10 ml. of malt infusion are added, and after half an hour the contents of the flask are boiled, cooled, made up to 250 ml. and filtered. Two hundred millilitres of the filtrate are heated on a boiling water-bath for 2½ hours with 15 ml. of 25 per cent. hydrochloric acid. After cooling and neutralising, the dextrose present is estimated by one of the standard methods, the conversion factor 0.90 being used to calculate the weight of starch present in the sample. A correction is made for the reducing power of the malt extract, which is determined separately.

R. P. Walton and M. R. Coe⁶⁵ have worked out a method in which the insoluble non-starchy material present in the products of diastatic hydrolysis are removed by filtration, the pectin being

precipitated by 60 per cent. alcohol, which does not precipitate the dextrins present. This method has been adopted by the Association of Official Agricultural Chemists.⁶⁶ The precautions to be taken in this work are contained in the preliminary papers by these workers.⁷¹⁻⁷³ Hartmann and Hillig⁶⁷ suggest that starch products containing much protein matter should be digested overnight with pepsin, a process which would destroy the proteins that occlude starch and at times render results unreliable. P. Fleury and G. Boyeldieu⁸¹ determine starch in bread prepared for diabetic patients by hydrolysing with dilute sulphuric acid and precipitating the proteins by the addition of an acid solution of mercuric sulphate which they claim to be better for this purpose than lead acetate. The dextrose remaining is then determined by polarimetric or reduction methods. A. Hock⁶⁹ uses diastase followed by acid treatment, but his chief modification is connected with the adequate removal of fats, protein and water-soluble substances that may interfere.

When starch hydrolysates contain dextrins the determination of maltose by chemical methods may give high results. A. S. Schultz, R. A. Fisher and co-workers¹²⁸ have determined the maltose in such products by fermenting the sugar with yeast. During acid hydrolysis of starch the highest maltose content they found was 25.2 per cent. by the fermentation method whereas chemical methods indicated 43-47 per cent. which, they consider, indicates a lack of specificity in the latter methods.

Herd and Kent-Jones,⁶ surveying the field of enzymes for use in the determination of starch, point out that the difficulties arising from the various methods proposed for the determination of starch in natural materials may be summarised as follows:—

1. Acid hydrolysis: presence of other hydrolysable carbohydrates.
2. Hydrolysis by prepared diastase: variable hydrolytic powers and the unknown action on various components of the starch.
3. Hydrolysis by malt diastase: variable hydrolytic action on hemicelluloses.
4. Hydrolysis by barley diastase: as 3; and in addition, it is also necessary to assume that the ratio amylose/maltose for other starches is the same as for potato starch.

A survey of methods for the determination of starch has been carried out by M. P. Etheridge.¹¹⁷

The investigation included the official American methods of hydrolysis with hydrochloric acid and with diastase and acid, and the Hopkins modification,¹¹⁶ of the Mannich-Lenz calcium chloride method.³⁵ Pure corn, wheat and potato starches

were used, their moisture, ash and protein-contents being determined and a rough estimate of the starch obtained by difference. For the determination of the moisture, the results obtained by drying for 24 hours in a Freas oven at 105-106° C. compared favourably with those given by drying *in vacuo* for a shorter period. Natural materials, such as cake flour, whole wheat flour and whole Lima beans, were also used. When the calcium chloride method was applied to these, the samples were washed on filter paper, instead of being centrifuged with alcohol, as recommended by Hopkins. Contrary to statements in the literature, this worker found that all the starch in the reputed pure and commercial starches was not obtained either by hydrolysis with hydrochloric acid or by diastase treatment followed by acid hydrolysis. The results were even lower than the 96 to 97 per cent. of the total starch found by Noyes *et al.*⁴⁷ On the other hand, with natural materials the diastase and hydrochloric acid method (a) gave fairly concordant results comparing better with those obtained by the calcium chloride method (b). Thus the following mean percentages were found: cake flour, (a) 72.87, (b) 75.90; whole wheat flour, (a) 66.95, (b) 67.29; rice bran, (a) 6.84, (b) 8.22; corn meal, (a) 62.44, (b) 63.76; whole rice, (a) 71.75, (b) 77.31; Lima beans, (a) 45.56, (b) 42.54. In most instances the calcium chloride method was very satisfactory with the pure starches. The Hopkins modification seemed to be the most promising single method and, by careful control of heating and the use of accelerated filtration, can be advantageously applied to natural materials. Other chemicals were tried as dispersing agents in an effort to prevent filtration difficulties. The use of calcium nitrate and sodium salicylate showed possibilities, although the dispersions were still difficult to filter. On the other hand, sulphosalicylic and formic acids gave promising results, and the dispersions could be readily filtered.

A comprehensive résumé of methods for determining starch is given by Herd and Kent-Jones,⁶ R. Kutscha,⁷⁷ O. Wolff,⁷⁸ K. Alpers,⁷⁹ and additional information has been classified for convenience under products in Table XXIV. (See p. 373.)

In order that readers may gain some idea of the composition of various starch-bearing materials the following table has been compiled from different sources. It must naturally be assumed that the figures given in the latest work are the most reliable and based on up-to-date analytical methods, but the original papers should be consulted in special cases to ascertain the method used, bearing in mind the comments made in the preceding pages.

TABLE XXIV

Determination of Starch in Various Materials
(See also 'Additional References'.)

<i>Product.</i>	<i>Type of Method Used.</i>	<i>Reference.</i>
Adhesives	Various methods discussed.	Nagel, <i>Zeit. Spiritusind.</i> , 1920, 43 , 129.
Barley	A number of methods reviewed, Lintner's preferred. Polarimetric method. Ewers' method. Effect on pentosans evaluated.	Ref. 77. C. J. Lintner, <i>Zeit. gesam. Brauw.</i> , 1911, 34 , 301. G. Fertman and V. Rudzevich, <i>Spirto-Vodochnaya Prom.</i> , 1939, No. 6, 37; <i>Khim. Referat Zhur.</i> , 1939, No. 11, 66.
Beet leaves	Iodine coloration.	G. Rowland, <i>Pub. inst. belge amélioration betterave</i> , 1939, 7 , 463.
Cocoa	Ewers' method satisfactory. Volumetric iodide method (see also p. 259). Lintner's cold polarimetric method. Sulphuric acid hydrolysis then sugar estimated by Fehling's method. Takadiastase followed by polarimetric or copper reduction estimation of sugar formed.	W. Greifenhagen, <i>Biochem. Zeit.</i> , 1911, 35 , 194. W. Whale. ⁶⁸⁻⁸⁰ G. Savini, <i>Chem. Zentralbl.</i> , 1923, 4 , 804. P. Trojanowsky, <i>Arch. Pharm.</i> , 1887, 210 , 30; W. L. Dubois, <i>U.S. Dept. Agric. Bur. Chem.</i> , 1909, <i>BULL.</i> 122 , 214; <i>BULL.</i> 132 , 136. C. Revis and H. R. Burnett, <i>Analyst</i> , 1915, 40 , 429.
Cassava flour	Ewers' method. Specific rotation of cassava starch, $[\alpha]_D = 183 \cdot 1$.	Riechelmann, <i>Zeit. offentl. Chem.</i> , 1921, 27 , 5.
Cattle foods	Saccharification with malt then estimate sugar by Fehling's solution.	P. L. Hibbard, <i>J. Amer. Chem. Soc.</i> , 1895, 17 , 64.
Cereals	Saccharification with malt then estimate sugar by Fehling's solution.	C. O'Sullivan, <i>J. Chem. Soc.</i> , 1884, 45 , 1.
Cinnamon	Ewers' method (see under Cocoa).	Greifenhagen (see Cocoa).
Confectionery (peach and apricot kernels)	Polarimetric method.	J. Grossfeld, <i>Zeit. unters. Lebensm.</i> , 1927, 53 , 156.
Fæces	Extract with CaCl_2 , ppt. with alcohol, hydrolyse, determine glucose by Kolthoff's iodometric method.	J. Terrier and J. Deshussies, <i>Mitt. Lebensm. Hyg.</i> , 1940, 31 , 249.
Farinas (various)	von Fellenberg's method gives low results. Ewers' method preferred for baked products.	J. Terrier, <i>ibid.</i> , 1940, 31 , 305; 1941, 32 , 59.

TABLE XXIV—(Continued)

<i>Product.</i>	<i>Type of Method Used.</i>	<i>Reference.</i>
Flour	Ewers' method.	J. Gerum, <i>Zeit. unters. Nahr.-u. Genussm.</i> , 1919, 37 , 145.
Flours (patent and granular) and whole grains	Extract with CaCl_2 sol. contg. acetic acid. Boil. Clarify with SnCl_4 or Uranyl acetate dissolved in CaCl_2 , sol. Filter. Polarise.	K. A. Clendenning, <i>Can. J. Res.</i> , 1945, 23B , 239.
Fodder	Ewers' method and Lintner's method (see Cattle foods).	A. Scholl, <i>ibid.</i> , 1909, 18 , 157.
Gluten	Polarimetric method.	P. Fleury and G. Boyeldieu, <i>J. Pharm. Chem.</i> , 1928, 7 , 207, 248.
Grain	Modified Ewers' method.	K. Musolin, <i>Spirto-Vodoch-naya Prom.</i> , 1937, 14 , Nos. 10-11, 59; <i>Chem. Zentr.</i> , 1938, II , 973.
	Specific gravity method. Table used to calculate starch-content.	V. Ershov, <i>Brodil'naya Prom.</i> , 1935, 12 , No. 6, 50; <i>Chem. Zentr.</i> , 1937, I , 2486.
	Uses petroleum in Ershov's method. Limited in scope.	R. Goldfarb, <i>Spirto-Vodoch-naya Prom.</i> , 1937, 14 , No. 8, 34; <i>Chem. Zentr.</i> , 1938, II , 202.
	Comparison of methods. Polarimetric methods considered most suitable.	M. V. Jonescu and H. Slusanschi, <i>Anuar. Inst. tercetari Agron. Român.</i> , 1937, 9 , 160; <i>Chem. Zentr.</i> , 1938, II , 3028.
	Extract with 1.86% HCl. and hydrolyse to glucose with stronger HCl. Determine glucose by Lane and Eynon's method. Results 1% higher than with polarimeter.	
Grain meal	Precipitation of starch as barium starch.	A. von Asboth, <i>Chem. Ztg.</i> , 1889, 13 , 591, 611.
Grains, spent	Iodine coloration or precipitation with iodine.	H. Weiss, <i>Zeit. gesam. Brauw.</i> , 1922, 45 , 122.
Green leaves	Iodine method.	J. J. Chinoy, <i>Analyst</i> , 1938, 63 , 876.
Grist	Extract with HCl. Hydrolyse with salivary amylase. Estimate sugar by oxidation with ferricyanide and titration with ceric sulphate.	W. Z. Hassid, R. M. McCready and R. S. Rosenfels, <i>Ind. Eng. Chem. (Anal. Ed.)</i> , 1940, 12 , 142.
	Successive hydrolysis by malt and acid and the sugar estimated.	R. Chrzaszcz, <i>Zeit. unters. Nahr.-u. Genussm.</i> , 1924, 48 , 306.
	Iodine colorimetric method.	C. Griebel and M. Nothnagel, <i>ibid.</i> , 1925, 49 , 352.
Marmalades		M. van Aerde, <i>Chem. Zentralbl.</i> , 1923, 4 , 890.
Margarine	Hydrolyse with H_2SO_4 , add pot. ferrocyanide and zinc acetate and estimate sugar by Fehling's solution.	

TABLE XXIV—(Continued)

Product.	Type of Method Used.	Reference.
Meat products	Iodine colorimetric method.	G. Ambuehl and H. Weiss, <i>Mitt. Geb. Lebensm.</i> , 1922, 13 , 170.
	Dissolve in KOH, ppt. starch with alcohol, hydrolyse and estimate sugar with Fehling's solution. (Factor—0.9.)	T. M. Price, <i>U.S. Dept. Agric. Bur. Anim. Chem.</i> , 1912, Circular 203, 6.
(Sausages, etc.)	Rapid polarimetric method.	O. Braadlie and A. Moen, <i>Tids. Kjemi Bergvesen</i> , 1940, 20 , 17.
" ,)	Acid dispersion and polarimetric determination of starch.	V. Jahn. ⁸³
Sausages and meat products	Treat with alcoholic KOH, filter: extract starch in residue with 5.7 N HCl, ppt. with EtOH, filter, dry and weigh.	W. C. McVey, <i>J. Assoc. Off. Agric. Chem.</i> , 1941, 24 , 928.
Oats porridge	See Toasted wheat flakes. Various methods reviewed.	H. Frankenbach, <i>Papier, Fabr.</i> , 1922, 20 , 1173.
Paper	Hydrolyse with HCl and estimate sugar with Fehling's solution. Spectrophotometric curves of iodine coloration.	V. Voorhees and O. Kamm, <i>Paper</i> , 1919, 24 , 1091.
	See also	L. E. Simerl and B. L. Browning, <i>Ind. Eng. Chem. (Anal. Ed.)</i> , 1939, 11 , 125.
		H. A. Bromley, <i>Paper</i> , 1915, 16 , 13; O. Kamm and H. Tendick, <i>ibid.</i> , 1919, 24 , 1091.
Paper	Extract with boiling 2.5% acetic acid; hydrolyse extract with HCl and titrate glucose formed. Mannose not dissolved by this method.	J. W. Dijk, <i>Chem. Weekblad.</i> , 1941, 38 , 329.
Pectin juices	Colorimetric iodine method.	H. Eckart, <i>Chem. Zentralbl.</i> , 1925, 2 , 2106.
		G. Perrier, <i>Ann. falsif.</i> , 1924, 17 , 208.
Pepper	Lintner's or Ewers' method. Polarimetric method.	A. Scholl (see Fodder) and Greifenhagen (see Cocoa), E. von Raumer, <i>Zeit. angew. Chem.</i> , 1893, 6 , 453.
Plant materials (see also Green leaves and Vegetable foods)	Saccharify with salivary amylase and estimate sugar by oxidation with ferricyanide combined with cerate titration.	W. Z. Hassid, R. M. McCready and K. J. Rosenfels, <i>Ind. Eng. Chem. (Anal. Ed.)</i> , 1940, 12 , 142.
Potatoes	Approximate-starch content from S.G.	Rathsack, 112, Sprockhoff, <i>Z. Spiritusind.</i> , 53 , 35.

TABLE XXIV—(Continued)

Product.	Type of Method Used.	Reference.
Freshly dug sweet potato	Diastatic hydrolysis and sugar determination preferred to S.G. or polarimetric methods. Approximate analysis. Starch and moisture-content fairly constant. Estimate moisture and calculate starch-content. Polarimetric method. Ewers' method.	S. Ostanin, <i>Spirto-Vodoch-naya Prom.</i> , 1937, No. 2, 33; <i>Khim. Referat Zhur.</i> , 1938, No. 6, 137. W. D. Kimbrough, <i>Amer. Soc. Hort. Sci.</i> , 1940, 37, 846. R. Zima, <i>Chem. Listy</i> , 1940, 34, 81. G. Behr, <i>J. Landw.</i> , 1939, 87, 103.
Potato flakes	Ewers' method gives low values. The Parow-Neumann method best.	J. Stastný and J. Kozelka <i>Chem. Zentr.</i> , 1942, ii, 1637.
Frozen potatoes	Apparent increase in starch-content on thawing compared with unfrozen potatoes.	A. Antonov, <i>Spirto-Vodoch-naya Prom.</i> , 1939, 6, 36; <i>Khim. Referat Zhur.</i> , 1939, No. 11, 70.
Potato products	Ewers' method preferred. Iodine precipitation followed by oxidation (see p. 259).	A. Scholl (see Fodder). G. Rankoff. ⁸⁴
Rice	Lintner's method. Precipitation as barium starch.	H. Schreib, <i>Zeit. angew. Chem.</i> , 1888, 1, 694. A. von Asboth. ²⁸
Sardine paste	Starch rendered accessible with cuprammonium solution.	F. Kaulfersch, <i>Zeit. Unters. Nahr-u. Genussm.</i> , 1920, 39, 344.
Soda crackers	(See Toasted wheat flakes.)	
Sweet potatoes	Ppt. starch iodide, recover starch, reppt., again recover, ppt. with alcohol and disperse in CaCl_2 sol. Ppt. proteins with uranyl-acetate and detm. optical rotation. $[\alpha]_D = 200.9$.	E. T. Steiner and J. D. Guthrie, ¹⁴⁰
Toasted wheat flakes	Modified Mannich-Lenz polarimetric method better than the Lintner-Schwarz method.	C. G. Hopkins, <i>J. Assoc. Off. Agric. Chem.</i> , 1940, 23, 489; <i>ibid.</i> , 1939, 22, 525.
Textiles	Extraction with cold HClO_4 add I_2 sol. and examine in photoelectric colorimeter with red filter.	R. L. McEwen, <i>Amer. Dye-stuff Rep.</i> , 1943, 32, 371.
Vegetable foods	Takadiastase followed by acid hydrolysis, then colorimetric determination of sugar by picrate method.	V. C. Myers and H. M. Croll, <i>J. Biol. Chem.</i> , 1921, 46, 537; M. R. Coe and G. L. Bidwell, <i>J. Assoc. Off. Agric. Chem.</i> , 1923, 7, 297; W. Thomas, <i>J. Amer. Chem. Soc.</i> , 1924, 46, 1670.
Vegetable foods	Disintegrate, extract with 4.0-8.0 M. HClO_4 then as for Textiles (above).	J. P. Nielson, <i>Ind. Eng. Chem. Anal.</i> , 1943, 15, 176.

TABLE XXIV—(Continued)

<i>Product.</i>	<i>Type of Method Used.</i>	<i>Reference.</i>
Vegetable preserves	Hydrolyse with diastase and estimate sugar with interferometer.	O. Wolff, <i>Zeit. angew. Chem.</i> , 1924, 37 , 206.
	Sample first heated with strong NH_4OH , then diastatic method employed.	F. Tempus, <i>J. Soc. Chem. Ind.</i> , 1923, 42 , 992.
	Consecutive extractions with hot water until extract gives no iodine reaction. ppt. starch from extract as starch-iodide.	T. von Fellenberg, <i>Mitt. Lebensm., Hyg.</i> , 1930, 21 , 78; <i>Chem. Zentr.</i> , 1930, i, 3114.

TABLE XXV—ANALYSES OF STARCH-BEARING MATERIALS

Material.	Water.	Starch.	Fibre.	Protein.	Fat.	Ash.	Sugar.	Gluten.	Carbo- hydrates not Fibre.	Reference.
Acorns, whole . . .	13.0	70	3.0	—	2.0	5.8	10	—	—	87.
Arrowroot . . .	13.17	81.85	small	below 1.0	small	small	—	—	—	—
Arrowroot, tubers . . .	62.9	25.30	—	1.56	0.26	1.23	2.8-4.1	—	—	—
Avocado seed.										
Mexican variety. Undried basis . . .	51.86	27.54	3.76	2.38	1.0	1.24	—	3.50	—	119.
Dry weight basis . . .	—	57.21	9.08	5.72	2.07	4.98	—	7.31	—	
Forté variety. Undried basis . . .	50.56	29.60	3.65	2.45	1.1	1.39	—	2.21	—	
Dry weight basis . . .	—	59.87	7.28	4.95	2.21	2.70	—	4.47	—	
Barley . . .	6.47	62.09	3.81	11.52	2.67	2.87	7.02	—	—	
American . . .	10.85	—	3.85	11.0	2.25	2.50	—	—	69.5	Wiley, quoted by Kent-Jones 88.
English . . .	14.3	—	4.5	10.6	2.1	2.5	—	—	66.0	Warrington, quoted by Kent-Jones 88.
feeding . . .	14.3	—	5.0	12.0	2.4	2.6	—	—	63.7	92.
" average . . .	14.0	—	4.5	11.0	1.5	2.5	—	—	66.5	88.
German . . .	14.3	—	3.9	9.4	2.1	2.5	—	—	67.8	Bell quoted by Jago 89.
long-eared . . .	13.06	63.51	7.28	11.46	1.03	2.32	1.34	—	76.7	90.
Pearl . . .	12.7	—	0.8	7.4	1.2	1.2	—	—	—	93.
Beans . . .	88.82	7.28	1.46	1.40	0.1	0.94	—	—	48.3-	
" haricot . . .	14.4	—	4.2	20.6-	1.1-2	3.35-	—	—	55.93	94.
Buckwheat flour . . .	15.7	—	5.35	26.7	—	3.95	—	—	75.9	90.
Bulrush millet . . .	14.0	—	0.6	7.1	1.2	—	—	—	—	93.
Canavalia sp. seeds . . .	12.29	68.60	5.31	7.54	3.37	2.89	—	—	—	95.
Cannab sp. seeds . . .	13.78	44.84	8.58	23.45	3.54	3.58	2.23	—	—	M. H. French 100.
Canna tubers (dried) . . .	—	—	3.39	3.6	0.78	7.45	—	—	84.78	
Cassava . . .	67.83	—	0.71	0.81	0.58	0.44	—	—	29.63	93.
" Mambo Leo, East Africa . . .	63.7	25.19- 26.5	—	2.46	0.08	—	1.07	—	—	102.
" flour . . .	12.9	—	1.91	2.18	1.58	1.91	—	—	80.24	
" starch . . .	12.14.8	—	—	1.0-1.9	0.86-	0.9-2.4	—	—	—	
" meal . . .	9.22	—	8.14	2.01	0.49	1.91	—	—	78.2	96.
Cowpeas . . .	12.16	81.89	—	0.2-0.9	—	0.8-1.0	—	—	—	
" starch . . .	10.88	—	4.94	26.82	1.10	3.91	—	—	53.35	93.
" starch . . .	10.20	39.20	3.12	28.81	3.01	2.98	—	—	50.32	114.
Gram, black, hunked . . .	12.02	87.30	—	Trace	mil	0.14	—	—	—	114.
" green . . .	13.41	—	0.01	22.99	1.12	3.05	—	—	59.42	93.
Ground durum, flour . . .	12.08	—	3.33	21.7	0.96	4.23	—	—	57.70	88.
	13.5-	—	—	10.2-	—	0.42-	1.77-	11.1-	—	
	14.4	—	—	13.6	—	0.61	2.75	11.94	—	

TABLE XXV—Continued

Material.	Water.	Starch.	Fibre.	Protein.	Fat.	Ash.	Sugar.	Gluten.	Carbo- hydrates not Fibre.	Reference.
Guinea corn	9.38	—	1.31	7.57	3.92	2.89	—	—	74.93	93.
Lentils	14.0	—	3.4	25.5	1.9	5.0	—	—	52.2	90.
"	15.0	55.3-	—	26.45-	—	2.94-	—	—	—	97.
"	68.2	—	—	33.3	—	3.8	—	—	—	
Maize	12.81	—	1.2	7.2	3.99	1.04	—	—	73.76	93.
"	12.34	64.66	1.86	14.27	3.58	1.35	1.94	—	—	Bell via Jago 89.
"	9.34	66.91	1.41	10.8	5.54	1.54	2.18	—	—	Richardson via Jago 89.
" embryo	—	—	2.9	21.7	29.6	11.1	—	—	34.7	
" endosperm	—	—	0.6	12.2	1.5	0.7	—	—	85.0	88.
" flour, average	12.5	66.78	0.9-1.8	7.0-9.5	1.5-3.5	0.6-1.3	—	—	—	
" hull	—	—	16.4	6.6	1.6	1.3	—	—	74.1	
" starch	12.15	84.87	—	0.2-0.5	0.02-0.1	0.1-0.5	—	—	—	
" whole	9.14	54.72	1.7	12.6	4.3	1.5-1.7	—	—	—	
Oats	6.92	56.91	1.29	14.27	7.87	2.22	6.07	—	—	Richardson via Jago 89.
" English	11.86	49.78	13.53	14.67	5.14	2.66	2.36	—	—	Bell via Jago 89.
" feeding, Canadian	10.0	61.1	7.5	12.75	5.4	3.17	—	—	—	Dyer via Kent-Jones 88.
" feeding, English	9.97-	53.3-	6.8-	8.65-	3.32-	2.57-	—	—	—	
"	15.97	63.0	11.9	14.3	5.86	3.78	—	—	60.23	
" grain	13.4	—	8.96	9.46	5.33	2.62	—	—	52.20	Berry via 88.
" husk	6.77	—	33.45	2.45	1.27	3.86	—	—	63.47	
" kernel	13.4	—	1.33	12.34	7.73	1.83	—	—	65.9	Hutchinson via 88.
" meal	7.2	—	3.5	14.2	7.3	1.9	—	—	66.0	88.
" average	8.5	—	1.5	14.0	8.0	1.8	—	—	64.8	Hutchinson via 88.
" rolled	7.2	—	3.5	15.4	7.2	1.9	—	—	21.01	
Potatoes	74.98	—	0.69	2.08	0.15	1.09	—	—	2.5	99.
"	76	16.23	—	2.0	—	1.0	—	—	22.85	Moore and Partridge 103.
"	74.0	—	—	2.0	0.15	1.0	—	—	15.98-	Leach 104.
"	66.1-	—	0.37-	1.43-	—	0.44-	—	—	30.53	
"	80.6	—	0.68	2.81	—	1.18	—	—	14.05-	
"	75.37-	—	0.28-	1.14-	0.02-	0.78-	—	—	20.37	
"	82.15	—	0.85	2.98	0.18	1.16	—	—	Average	
"	Average	—	Average	Average	Average	Average	—	—	17.36	
"	78.89	—	0.56	2.14	0.10	0.95	—	—	13.3-	Winton 105.
"	67.8-	—	0.28-	1.1-3.0	0.0-2	0.5-1.9	—	—	26.5	
"	84.0	—	0.90	Average	Average	Average	—	—	18.4	
"	Average	—	Average	Average	Average	Average	—	—	—	
"	78.3	—	0.4	2.2	0.1	1.0	—	—	—	

TABLE XXV—Continued

Material.	Water.	Starch.	Fibre.	Protein.	Fat.	Ash.	Sugar.	Gluten.	Carbo- hydrates not Fibre.	Reference.
Potatoes	71.99- 82.18 Average 77.41	—	0.5-0.76 Average 0.61	1.37- 2.2 Average 1.66	0.025- 0.185 Average 0.056	0.87- 1.185 Average 1.01	—	—	14.39- 24.58 Average 19.12	Schrader 106.
"	75.9	20.8	—	1.3	0.11	0.72	—	—	22.85	} Carpentier 107. Singh and Mathur 108. Mangold 109.
"	79.3	18.4	—	2.0	0.10	0.64	—	—	19.19	
"	80.8	13.4	—	2.37	—	1.3	—	—	—	
"	72-82.2	—	0.49- 0.76	1.42- 2.2	0.02- 0.18	0.87- 1.18	—	—	14.6- 24.6	
"	79.18- 81.3 Average 79.98	12.88- 16.13	0.42- 0.56 Average 0.51	2.31- 2.77 Average 2.63	0.07- 0.12 Average 0.09	0.94- 1.10 Average 1.03	—	—	13.32- 16.56 Average 15.6	} Headdon 110. Goldthwaite 111.
"	78.78	14.56	0.50	2.74	0.09	1.02	—	—	15.88	
"	81.85	11.35- 21.81	—	0.87- 3.19 Average 2.02	—	0.63- 1.52 Average 0.95	—	—	13.93- 25.62 Average 19.79	
"	77.23	16.02	—	1.787-	—	0.87-	—	—	16.72-	
"	73.55- 80.51 Average 77.12	13.6- 17.68	—	3.1	—	1.29	—	—	22.56	
"	71.8- 81	15.43 20.3	1.20- 2.58	2.31	—	1.073	—	—	19.49	Rathsack 112.
"	75.68- 79.96 Average 75.8	13.19- 18.03	—	2.13- 2.52 Average 2.1	—	0.88- 1.02	—	—	—	Metzger 113.
" peeled	75.8	18.27	—	2.1	Trace	—	—	—	—	Leach 104. See also 101. Hutchinson via 88.
Rice	10-14	70.80	—	6.9	0.5	0.4-2.0	—	—	15.95- 30.53 Average 0.5-1.5	
" flaked	11.7	—	—	7.9	0.5	0.4	—	—	79.5	
" husked, average	11.68	—	0.7	7.71	1.19	0.93	—	—	77.79	
" Burma	12.38	—	0.85	7.24	1.52	1.13	—	—	76.88	Bull. Dept. Agric., U.S.A., 1916.
" Carolina	12.15	77.66	Trace	9.34	0.19	0.28	—	0.38	—	Bell via Jago 89.
" Honduras	12.32	—	0.99	8.57	1.79	1.18	—	—	75.15	Bull. Dept. Agric., U.S.A., 1916.
" polished	13.24	—	0.33	6.31	0.38	1.60	—	—	78.14	
" average	12.9	—	0.25	6.47	0.46	0.49	—	—	79.43	
" Burma	12.82	—	0.29	6.61	0.22	0.32	—	—	70.74	
" Honduras	11.89	—	0.3	8.06	0.25	0.36	—	—	79.14	Bull. Dept. Agric., U.S.A., 1916.

TABLE XXV—Continued

Material.	Water.	Starch.	Fibre.	Protein.	Fat.	Ash.	Sugar.	Gluten.	Carbo- hydrates not Fibre.	Reference.
Rice, skinned, average	13.02	—	0.68	6.9	2.24	1.44	—	—	75.71	99.
" " Burma	13.38	—	0.29	6.59	6.3	0.40	—	—	79.03	{ Bull. Dept. Agric., U.S.A., 1916.
" " Honduras	12.5	—	0.30	7.88	0.28	0.47	—	—	78.57	
" " unhusked, average from different sources	12.55	—	7.84	6.35	2.14	5.93	—	—	65.19	99.
" " unhusked, Honduras	11.27	—	8.67	7.48	1.58	5.4	—	—	65.6	{ Bull. Dept. Agric., U.S.A., 1916.
" " unhusked, Japan	11.25	—	7.93	6.5	1.74	5.14	—	—	66.19	Bell via 89.
Rye	12.45	61.87	3.23	14.87	1.43	1.85	—	4.30	—	Richardson via 89.
" " German	8.85	61.87	1.47	11.6	1.83	2.06	—	7.57	—	
" " "	12.64	—	—	3.74	—	0.4	—	—	—	{ Morrison, 1926, via 88.
" " flours	14.5	—	—	7.4	—	1.32	—	—	—	
" " "	9.82	—	—	6.72	—	0.64	—	—	—	
" " "	13.35	—	—	14.04	—	2.07	—	—	—	
Sago flour	12.17	81.87	0.1-0.4	0.1-1.0	0.1-0.4	0.1-0.7	—	—	—	Lane and Eynon.
" " Sweet potato	11.7	—	0.13	0.13	0.13	0.35	—	—	87.56	99.
Tapioca	11.01	15.99	0.17	1.40	0.22	1.21	—	—	93.	99.
Taro, Hachae (dry weight basis)	12.7	—	4.87	0.88	0.23	0.85	—	—	80.47	Very complete analysis given 115.
Wheat	7.75	77.91	1.42	2.0	0.56	1.55	—	0.52	—	
" " Barusso (Bahia)	9.25	67.88	1.9	11.03	2.30	1.84	—	3.5	—	
" " "	13.7	—	—	10.03	—	0.39	10.01-	1.37-	—	
" " "	15.06	—	—	12.03	—	0.41	13.0	1.65	—	88.
" " Manitoaba	10.3	—	—	10.2	—	—	—	1.0-	—	
" " "	15.2	—	—	15.0	—	—	—	2.58	—	
" " average	12.7	—	—	12.8	—	—	—	1.85	—	
" " spring	14.08	65.86	2.93	11.59	1.56	1.74	—	2.24	—	
" " winter	12.08	63.71	3.03	15.53	1.48	1.60	—	2.57	—	{ Bell via 89.
" " flour, Australian	12.13	—	—	9.06	—	0.37	9.4-	1.52-	—	
" " "	13.8	—	—	10.89	—	0.50	11.53	2.32	—	
" " English	12.42	—	—	7.81	—	0.33	8.15-	1.0-	—	
" " "	15.47	—	—	10.03	—	0.44	10.48	1.63	—	
" " Manitoaba	14.4	—	—	10.2	—	0.37	10.85-	1.34-	—	88.
" " "	15.79	—	—	13.6	—	0.45	14.16	1.94	—	
" " Russian	14.49	—	—	8.89	—	0.34	9.75-	1.18-	—	
" " "	15.87	—	—	11.17	—	0.44	11.67	1.66	—	
" " "	13.7	—	—	7.75	—	0.37	8.06-	1.09-	—	
" " Yeoman	16.35	—	—	11.12	—	0.46	11.56	1.97	—	

REFERENCES

1. A. LECLERC, *J. pharm. chim.*, 1890, **21**, 641.
2. P. BIOURGE, *Zeit. ges. Brauw.*, 1908, **31**, 277.
3. O. RASK, *J. Assoc. Off. Agric. Chem.*, 1927, **10**, 108 and 473.
4. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 'Official and Tentative Methods of Analysis', 1930.
5. A. R. LING and F. E. SALT, *J. Inst. Brewing*, 1931, **37**, 595.
6. C. W. HERD and D. W. KENT-JONES, *J. Soc. Chem. Ind.*, 1931, **50**, 15T.
7. L. JONES, *J. Assoc. Off. Agric. Chem.*, 1932, **15**, 582.
8. O. S. RASK, *ibid.*, 1927, **10**, 473.
9. F. E. DENNY, *Contrib. Boyce Thompson Inst.*, 1934, **6**, 381.
10. W. H. KRUG and H. W. WILEY, *J. Amer. Chem. Soc.*, 1898, **20**, 266.
11. J. MAYRHOFER, *Forsch. Ber. Lebensm.*, 1896, **3**, 141 and 429.
12. M. PIETTRE, *Seventh Int. Congr. Appl. Chem.*, 1909, p. 291.
13. G. BAUMERT and H. BODE, *Zeit. angew. Chem.*, 1900, **13**, 1074 and 1111.
14. G. BAUMERT, *Zeit. Nahr. Genussm.*, 1909, **18**, 167.
15. P. BEHREND and H. WOLFS, *Zeit. angew. Chem.*, 1901, **14**, 461.
16. A. KAISER, *Chem.-Ztg.*, 1902, **26**, 180.
17. TH. VON FELLEBERG, *Mitt. Lebensm. Hyg.*, 1916, **7**, 369.
18. — *ibid.*, 1917, **8**, 55; 1928, **19**, 51.
19. J. J. CHINOY, F. W. EDWARDS and H. R. NANJI, *Analyst*, 1934, **59**, 673.
20. H. ECKART, *Chem. Zell. Gewebe*, 1925, **12**, 243.
21. W. S. LONG, *Trans. Kansas Acad. Sci.*, 1916, **28**, 172.
22. H. WEISS, *Zeit. ges. Brauw.*, 1922, **45**, 122.
23. J. C. SMALL, *J. Amer. Chem. Soc.*, 1919, **41**, 107, 113.
24. F. E. DENNY, *J. Assoc. Off. Agric. Chem.*, 1922, **6**, 175.
25. — *Contrib. Boyce Thompson Inst.*, 1934, **6**, 129.
26. J. T. SULLIVAN, *Ind. Eng. Chem. (Anal. Ed.)*, 1935, **7**, 311.
27. TIAN, *Bull. Soc. Chim. France*, 1923, **33**, 898.
28. A. VON ASBOTH, *Repert. Anal. Chem.*, 1887, **7**, 299; *Chem.-Ztg.*, 1887 **11**, 785; 1889, **13**, 591, 611.
29. C. MONHEIM, *Zeit. angew. Chem.*, 1888, **1**, 126 and 401.
30. A. BAUDRY, *Zeit. Spiritusind.*, 1892, **15**, 41.
31. — *Dingler's Polytechn. J.*, 1892, **285**, 238.
32. L. PELLET and MÉTILLON, *Bull. Assoc. Chim. sucr. distil.*, 1906, **24**, 1720.
33. J. EFFRONT, *J. Soc. Chem. Ind.*, 1896, **15**, 923.
34. D. CRISPO, *Ann. chim. anal.*, 1899, **4**, 290.
35. C. MANNICH and K. LENZ, *Zeit. Nahr. Genussm.*, 1920, **40**, 1; *Can. J. Res.*, 1934, **11**, 751.
36. C. J. LINTNER, *Zeit. ges. Brauw.*, 1907, **30**, 109.
37. O. WENGLEIN, *ibid.*, 1908, **31**, 53.
38. C. J. LINTNER, *Zeit. Nahr. Genussm.*, 1908, **16**, 509.
39. — *Zeit. angew. Chem.*, 1912, **25**, 1177.
40. M. CANET and O. DURIEUX, *Bull. Soc. chim. Belg.*, 1907, **21**, 329.
41. J. KÖNIG, W. GREIFENHAGEN, and A. SCHOLL, *Zeit. Nahr. Genussm.*, 1911, **22**, 714.
42. S. HALS and S. HEGGENHANGEN, *Landsw. Vers. Stat.*, 1917, **90**, 391.
43. E. EWERS, *Zeit. öffentl. Chem.*, 1905, **11**, 407; **14**, 8 and 150.
44. — *ibid.*, 1910, **15**, 8.
45. E. EWERS, *Zeit. ges. Brauw.*, 1915, **21**, 232.
46. — *ibid.*, 1908, **31**, 250.
47. W. A. NOYES, *et al.*, *J. Amer. Chem. Soc.*, 1904, **26**, 266.
48. W. A. DAVIS and A. J. DAISH, *J. Agric. Sci.*, 1913, **5**, 437; *ibid.*, 1914, **6**, 152.
49. G. S. FRAPS, *J. Assoc. Offic. Agric. Chem.*, 1932, **15**, 304.
50. A. R. LING, *J. Soc. Chem. Ind.*, 1923, **42**, 48T.
51. E. WALDESCHMIDT-LEITZ, M. REICHEL, and A. PURR, *Naturwiss.*, 1932, **20**, 254.
52. G. NORDH and E. OHLSSON, *Zeit. physiol. Chem.*, 1932, **204**, 89.

53. A. R. LING, D. R. NANJI, and W. J. HARPER, *J. Inst. Brewing*, 1924, **30**, 838.
54. A. R. LING and D. R. NANJI, *Biochem. J.*, 1923, **17**, 593.
55. G. A. VAN KLINKENBERG, *Zeit. physiol. Chem.*, 1932, **212**, 173.
56. T. C. TAYLOR and H. A. IDDLIS, *Ind. Eng. Chem.*, 1926, **18**, 713.
57. T. C. TAYLOR and R. P. WALTON, *J. Amer. Chem. Soc.*, 1929, **51**, 3431.
58. A. R. LING, *J. Inst. Brewing*, 1922, **28**, 828 and 851.
59. H. T. BROWN, *Trans. Guinness Res. Labs.*, 1903, **1**, 79.
60. H. T. BROWN and HERON, *Chem. Soc. Trans.*, 1879, **35**, 601.
61. S. NISHIMURA, *Chem. Zell. Gewebe*, 1925, **12**, 202.
62. W. A. DAVIS and A. J. DAISH, *J. Agric. Sci.*, 1914, **6**, 152.
63. I. D. COLLINS, *Science*, 1927, **66**, 430.
64. O. LEHMANN, *Planta*, 1931, **13**, 575.
65. R. P. WALTON and M. R. COE, *J. Agric. Res.*, 1923, **23**, 995.
66. M. R. COE, *J. Assoc. Offic. Agric. Chem.*, 1926, **9**, 147.
67. HARTMANN and HILLIG, *ibid.*, 1926, **9**, 482.
68. W. WHALE, *Analyst*, 1938, **63**, 328, 421.
69. A. HOCK, *Biochem. Zeit.*, 1937, 294, 336.
70. M. MAERKER, *Chem.-Ztg.*, 1885, **9**, 319.
71. R. M. COE, *J. Assoc. Offic. Agric. Chem.*, 1923-24, **7**, 341.
72. — *ibid.*, 1924-25, **8**, 358.
73. R. P. WALTON and R. M. COE, *ibid.*, 1923-24, **7**, 995.
74. H. LÜERS and F. WIENINGER, *Zeit. ges. Brauw.*, 1925, **48**, 35.
75. A. R. LING, E. H. CALLOW, and W. J. PRICE, *J. Soc. Chem. Ind.*, 1923, **42**, 48.
76. A. R. LING and W. J. PRICE, *J. Inst. Brew.*, 1923, **29**, 732.
77. R. KUTSCHA, *Woch. Brauer*, 1917, **34**, 277, 290, 294, 304, 313, 323, 332, 339, 350, 359, 368, 375, 381, 391, 398 and 406.
78. O. WOLFF, *Zeit. Spiritusind.*, 1924, **47**, 178.
79. K. ALPERS and H. ZIEGENSPECK, *Zeit. Unters. Nahr.-Genussm.*, 1923, **45**, 163.
80. W. WHALE, *Analyst*, 1939, **64**, 588.
81. P. FLEURY and G. BOYELDIEU, *Ann. Falsif.*, 1928, **21**, 124.
82. L. W. JIRAK, *Zeit. Spiritusind.*, 1935, **58**, 81.
83. V. JAHN, *Zeit. Unters. Lebensm.*, 1927, **53**, 262.
84. G. RANKOFF, *ibid.*, 1927, **53**, 138.
85. M. I. KNYAGINICHEV and V. K. PALILOVA, *Biokhimiya*, 1939, **4**, 423.
86. J. KAVČIČ, *Kolloidchem. Beih.*, 1930, **30**, 406.
87. S. SUGIZAKI, *J. Agric. Chem. Soc., Japan*, 1939, **15**, 1173.
88. D. W. KENT-JONES, 'Modern Cereal Chemistry,' 3rd ed., The Northern Publ. Co. Ltd., Liverpool, 1939.
89. W. JAGO and W. C. JAGO, 'The Technology of Breadmaking,' Simpkin, Marshall, Hamilton, Kent & Co. Ltd., 1911.
90. R. HUTCHINSON, 'Food and the Principles of Dietetics,' Arnold, London, 1927.
91. C. B. MORISON, *Baking Technol.*, No. **8**, 232.
92. T. B. WOOD, 'Farm Crops,' 1925, **1**, 248, Gresham Publ. Co. Ltd., London.
93. JOACHIM, *Trop. Agric.*, 1938, **90**, 3.
94. A. W. MARSDEN, *J. Roy. Agric. Soc.*, 1941, **66**, 98.
95. F. W. FRIESE, *Zeit. Unters. Lebensm.*, 1938, **75**, 566.
96. ANON, *Farming*, S. Africa, 1939, **14**, 404.
97. J. CARLES, *Compt. rend.*, 1940, **210**, 111.
98. R. A. BERRY, 'Farm Crops,' 1925, **1**, 188. Gresham Publ. Co. Ltd., London.
99. ANON, *Bull. Imperial Inst.*, 1917.
100. M. H. FRENCH, *Ann. Rep. Dept. Vet. Sci. Animal Husbandry, Tanganyika Territ.*, 1938. Pt. **2**, 37; Publ. 1939.
101. V. SADASIVAN and A. SREENIVASAN, *Indian J. Agric. Sci.*, 1938, **8**, 807. (Analyses of different varieties of rice.)

102. W. D. RAYMOND, W. JOJO and Z. NICODEMUS, *East Afric. Agric. J.*, 1941, **6**, No. 3, 154.
103. MOORE and PARTRIDGE, 'Aids to the Analysis of Foods and Drugs,' 1934.
104. LEACH, 'Food Inspection and Analysis,' Chapman & Hall, London, 1920, 282.
105. WINTON and WINTON, 'The Structure and Composition of Foods,' Vol. II, Chapman & Hall, London, 1935.
106. SCHRADER, *Arch. Tierernähr. Tierzucht*, 1933, **9**, 524; *Nutr. Abst. and Reviews*, 1933, **3**, 955.
107. BARKER, D. S. I. R., Food Invest. Board Rept., 1931, 78, H.M.S.O.
108. SINGH and MATHUR, *Ann. Appl. Biol.*, 1937, **24**, 469.
109. MANGOLD, via *Chem. Abst.*, 1936, **30**, 6840.
110. HEADDON, *Colo. Expt. Stat. Bull.*, 1924, **291**.
111. GOLDTHWAITE, *ibid.*, 1925, **296**.
112. RATHSACK, 'Der Speisewert der Kartoffel,' Berlin, 1935, 47.
113. METZGER *et al.*, *Proc. Am. Soc. Hort. Sci.*, 1937, **35**, 635.
114. J. L. GAVIN and M. H. QURESKI, *Ind. Eng. Chem.*, 1941, **33**, 640.
115. G. J. LEY, J. H. PAYNE and D. W. EDWARDS, *Hawaii Agric. Exp. Stat., Ann. Rept.*, 1937, 49.
116. C. G. HOPKINS, *Canad. J. Res.*, 1934, **11**, 751.
117. M. P. ETHERIDGE, *J. Assoc. Offic. Agr. Chem.*, 1941, **113**.
118. R. T. BALCH, *Ind. Eng. Chem. (Anal. Ed.)*, 1941, **13**, 246.
119. L. S. WEATHERBY and D. G. SORBER, *Ind. Eng. Chem.*, 1931, **23**, 1421.
120. J. KÖNIG, W. GREIFENHAGEN and A. SCHOLL, *Zeitsch. Nahr.-Genussm.*, 1911, **22**, 714.
121. L. EYNON and J. H. LANE, 'Starch,' Heffer & Sons Ltd., London, 1928.
122. G. BAUMERT, *Z. Nahr.-Genussm.*, 1912, **24**, 449.
123. M. P. ETHERIDGE, *J. Assoc. Offic. Agr. Chem.*, 1942, **25**, 621.
124. — *ibid.*, 1943, **26**, 214.
125. ASSOC. OFF. AGRIC. CHEM., *Methods of Analysis*, 1940, 359.
126. J. H. VAN DE KAMER, *Chem. Weekblad*, 1941, **38**, 286.
127. ANON., *Ind. Eng. Chem.*, 1941, **13**, 818.
128. A. S. SCHULTZ, R. A. FISHER, *et al.*, *Ind. Eng. Chem., Anal.*, 1943, **15**, 496.
129. K. A. CLENDENNING, *Canadian J. Res.*, 1942, **C20**, 403.
130. F. R. EARLE and R. T. MILNER, *Cereal Chem.*, 1944, **21**, 567.
131. R. W. KERR, 'Chemistry and Industry of Starch', Academic Press Inc., N.Y., 1944, p. 125.
132. K. H. MEYER, for a review of recent work see 'Recent Developments in Starch Chemistry,' in Kraemer, 'Advances in Colloid Science,' p. 143-182, New York, 1943. Also 'Natural and Synthetic High Polymers,' Vol. 4, p. 387-420, New York, 1942.
133. K. FREUDENBERG, FRIEDRICH and BUMANN, *Ann.*, 1932, **494**, 41.
134. C. G. HOPKINS, *Can. J. Res.*, 1934, **11**, 751.
135. C. J. LINTNER, *Z. Nahr. Genussm.*, 1907, **14**, 205.
136. M. P. ETHERIDGE, *J. Assoc. Offic. Agr. Chem.*, 1944, **27**, 404.
137. C. E. G. PORST and H. A. CROWN, *Ind. Eng. Chem.*, 1913, **5**, 304.
138. K. A. CLENDENNING and D. E. WRIGHT, *Canad. J. Res.*, 1945, **23**, B, 113.
139. — *ibid.*, 1945, **23**, B, 131.
140. E. T. STEINER and J. D. GUTHRIE, *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 736.
141. F. J. BATES *et al.*, Circ. C440, *Natl. Bur. Stds.*, Washington, 1942.
142. C. A. BROWNE and F. W. ZERBAN, 'Physical and Chemical Methods of Sugar Analysis,' 3rd edit., J. Wiley & Sons, N.Y., 1941.
143. J. N. BRONSTED, *Chem. Revs.*, 1928, **5**, 231.
144. C. F. POE and B. P. JUUKOLA, *Food Res.*, 1944, **3**, 338.

ADDITIONAL REFERENCES

- E. MUNSEY, *J. Assoc. Offic. Agric. Chem.*, 1937, **20**, 360. (Determination of starch in flour.)

- G. STEINHOFF, *Textilber. (Eng. Ed.)*, 1935, **16**, 73. (Specifications for potato starch.)
- H. LUEHRIG, *Pharm. Zentr.*, 1921, **62**, 141. (Ewers' method gives the most consistent results.)
- C. FAULENBACH, *Zeit. physiol. Chem.*, 1882, **83**, 510. (Enzymatic, followed by acid hydrolysis, then sugar estimated with Fehling's solution.)
- O. REINKE, *Zeit. anal. Chem.*, 1890, **29**, 472. (Similar method to Faulenbach's.)
- C. J. LINTNER and G. DÜLL, *Zeit. angew. Chem.*, 1891, **4**, 537. (Suggests factor of 0.94 to convert dextrose figure to starch.)
- E. HORTON, *J. Agr. Sci.*, 1921, **11**, 240. (Concludes use of taka-diastase in estimating starch requires control tests with each set of analyses.)
- A. DUERING, *Zeit. Unters. Nahr.-Genussm.*, 1924, **47**, 248. (Close agreement obtained between Ewers' method and Mayrhofer's gravimetric method.)
- A. LASERDA, *Rev. soc. brasilquím.*, 1938, **7**, 27. (Determination of starch in flour.)
- J. STRAUB and A. MIDDELBECK, *Chem. Weekblad.*, 1938, **35**, 743. (Chemistry of alkaline copper estimation of sugars discussed.)
- M. V. JONESCU and L. GAAL, *An. Inst. cerc. agron. Rom.*, 1936, **8**, 453. (Methods of estimating glucose compared.)
- V. DORFMAN, *Spirtovod. Prom.*, 1937, **14**, No. 3, 25. (Modified Maerker method for starch determination.)
- ANON, *Jokhels'son Voprosy Pitaniya*, 1937, **6**, No. 2, 99. (Determination of wheat and potato starches in sausage products.)
- C. G. HOPKINS, *J. Assoc. Offic. Agric. Chem.*, 1939, **22**, 523. (Compares methods of Chinoy (ref. 19), Mannich-Lenz (ref. 35) and Lintner-Schwarz (*Zeit. Brauw.*, 1913, Nos. 8 and 9), but draws no conclusions. (Chooses modification of last method.)
- SCHWONKE, *Zeit. Spiritusind.*, 1929, **52**, 198. (Sampling of damaged tubers.)
- B. LAMPE and W. KILP, *ibid.*, 1929, **52**, 199. (Sampling of damaged tubers.)
- W. E. STONE, *J. Amer. Chem. Soc.*, 1897, **19**, 183, 347. (Estimation of sugars and starch in foodstuffs described.)
- F. W. TRAPHAGEN and W. M. COBLEIGH, *ibid.*, 1899, **21**, 369. (Fehling's solution used and cuprous oxide dissolved in ferrous sulphate and sulphuric acid and titrated with potassium permanganate.)
- W. C. McVEY, *J. Assoc. Offic. Agr. Chem.*, 1941, **24**, 928. (Quicker and slightly more accurate method than *Assoc. Offic. Agr. Chem.*, 'Method of Analysis', 1940, 378, for starch in meat products.)
- W. KRÖNER *et al.*, *Z. anal. Chem.*, 1942, **1**, 277. (Relation between dry substance, refraction and density of starch hydrolysates.)
- C. L. HOFFPAUIR, *J. Assoc. Offic. Agr. Chem.*, 1949, **32**, 291. (Comparison of methods for determining starch in plant material. CaCl_2 extraction and measurement of starch-iodide colour satisfactory for 0.6 per cent. starch.)
- D. G. GRIFFITHS and N. A. POTTER, *Biochem. J.*, 1945, **39**, 423. (Determination of starch in frozen apple tissue. Takadiastase used.)
- O. S. RASK, *J. Assoc. Offic. Agr. Chem.*, 1947, **30**, 376. (Three modifications to tentative A.O.A.C. *Methods of Analysis*, 1945, p. 249, proposed.)
- D. M. HELLER, *ibid.*, 1947, **30**, 450. (Determination of starch in salad dressing and mayonnaise.)
- S. D. FINE, *ibid.*, 1948, **31**, 347. (Tentative method for starch in mayonnaise and salad dressing, *ibid.*, 1947, **30**, 74, sufficiently precise.)
- F. M. GARFIELD, *ibid.*, 1947, **30**, 446. (Starch determination in prepared mustard and mustard flour.)
- L. LARGARDE, *Bull. soc. chim.*, 1946, 665. (Colorimetric detm. of starch by iodine reaction.)
- F. J. VILES and L. SILVERMAN, *Analyt. Chem.*, 1949, **21**, 950. (Determination of starch by measurement of colour developed with anthrone in conc. sulphuric acid.)
- D. L. MORRIS, *Science*, 1948, **107**, 254. (Detm. of starch using anthrone reaction.)

- W. J. EVA and E. E. RANKIN, *Canad. J. Res.*, 1945, **23B**, 260. (Comparison of five methods. Hopkins' method the most precise, Clendenning's preferred for simplicity and rapidity.)
- K. A. CLENNING, *ibid.*, 1945, **23B**, 239. (Critical studies of polarimetric methods for detm. starch in whole-wheat, granular and patent flours.)
- M. P. ETHERIDGE, *J. Assoc. Offic. Agr. Chem.*, 1945, **28**, 492. (Detm. starch in raw and baked cereals. Clendenning procedure preferred for simplicity and ease.)
- MARINELLI, *Ann. Chim. applic.*, 1946, **36**, 46. (Hydrolysis of starch in flour with hydrochloric acid, d 1.19, at the boil, complete in 20 mins.)

CHAPTER 18

THE ANALYSIS OF DEXTRINS

A FACTORY may make dextrins either for sale or to be used as the raw material for manufacturing a product in some other part of the factory, but in either case the manufacture and the characteristics of the dextrins must be kept as near to standard as possible. This can be done only by means of constant checking at every stage of the process, from receiving the raw starch to packing the re-moistened dextrin produced from it. A purchased dextrin should be examined against a sample of standard dextrin known by previous experience to be suitable for the purpose in mind, and once a good source of supply is found, it is often preferable to deal exclusively with that firm.

If a sample of dextrin is received for matching purposes all the information possible should be obtained from the chemical and physical tests, but where a standard process is being worked, it is only necessary to carry out a few tests at the various stages of the process to determine the end-point of a particular operation. The tests in this case would include determinations of moisture in the raw starch, which should not exceed certain maxima, varying with the particular starch used, the iodine reaction and the viscosity of the dextrin in the roaster, the amount of sugar after roasting, and the amount of water present after re-moistening the dextrin. The following details are set forth merely as a groundwork for the examination of a dextrin for any particular purpose, and are not intended to cover every case which is likely to arise.

The analytical and physical examination of starch and dextrin has been dealt with by F. L. P. Krizkovsky.¹¹ W. Hönsch¹² states that the figure for the specific gravity of dextrin given in Beilstein's 'Handbuch der Organischen Chemie,' 1893, I, 1088, 3rd edition, is a misquotation, and finds that fine white dextrin has $D_{20}^{20} = 1.593$, fine yellow 1.527, superior yellow, thick-boiling 1.561, and thin-boiling 1.542. The specific gravity appears to vary with the method of preparation and the starch used, but a mean value of 1.556 may be assumed. In practice, however, the specific gravity of dextrin is rarely, if ever, required.

Appearance.—Dextrins which have been made by an acid treatment are invariably lighter in colour than those made by

merely roasting the raw starch, which produces products analogous to the dextrins known as British gums. The 'acid dextrins' are white, cream, yellow or buff powders, and those made by heat alone are brownish. A further modification is 'crystal gum,' which is a dextrin that has been dissolved, the solution treated with activated charcoal, filtered, and evaporated to dryness. This type of product resembles gum-arabic in appearance, and constitutes a special grade for use in very high-class work which can stand the extra price that its use entails. Some dextrins, made by one of the wet processes, appear as syrupy liquids, or as amorphous masses which have a flaky appearance due to their solution having been evaporated after the conversion on a drum- or a band-dryer.

The coloured varieties of dextrin are almost completely soluble in cold water, and invariably soluble in hot water, viscous pastes to slightly syrupy liquids being obtained according to the concentration and the degree of conversion. These solutions, on standing, sometimes show 'setback,' i.e. they thicken and develop cloudiness. In dilute solutions they may show a clear supernatant layer of liquid. Such dextrins are termed 'unstable,' and their use may cause trouble, especially when employed in adhesives for use on machines where the workability has been adjusted to an optimum value by means of careful formulation. Should such an adhesive increase in viscosity on standing, the other properties necessary for satisfactory running of the machine are thrown out of balance, and a poor performance on the part of the adhesive results. The cloudiness in this case is probably caused by the reversion of unconverted amylose, present as soluble starch, due to the conversion being carried out too rapidly.

The finer the quality of the starch used for the manufacture of the dextrin the better will be the appearance of the finished product. Thus good potato or tapioca starch will give a lustrous dextrin, and the lustre is greatly impaired if the starch used is inferior. The use of maize or wheat starch results in the production of a matt-looking dextrin, irrespective of the quality of the starch employed.

The acid used as the catalyst has some effect on the appearance of the dextrin made with its aid, and in general nitric acid imparts a reddish-yellow tinge, hydrochloric acid a yellow colour, whilst sulphuric acid, which is sometimes used, imparts a brownish tinge. The colour of the dextrin gives an approximate idea of the degree of conversion, but very little more information can be obtained without the use of a microscope.

Although the dextrin under examination may be soluble in

water, its dissolution can be impeded by the use of glycerol or glycol, or by suspension in alcohol. The effect of roasting upon the shape and structure of the starch grain can therefore be examined. The granules of the dextrin, if not too strongly converted, appear very similar to those of the starch from which it is made, but by adjusting the amount of glycerol and water it can be caused to disintegrate slowly. As mentioned on p. 320, the disintegration consists in the peeling off of layers, which float away and dissolve, and in this respect dextrins differ from soluble starches and can thus be differentiated from them. The dextrin so examined should be lightly stained with iodine to bring it into contrast with the rest of the field (see Photomicrograph No. 13).

An interesting example of the value of this method came to the notice of the author and is described on p. 314.

With dextrins in solution, or dried from solution, very little information as to the starch used can be obtained by the microscope, but in these cases the odour of the heated solution of the particular dextrin may assist, maize and potato products being readily identified.

The presence of black specks and dirt should be looked for, as their presence in excessive amounts renders a dextrin unsuitable for certain types of work, for example, in paper-surfacing. Tactile examination gives some information, as potato dextrins do not cling to the hand if dry, and are harsher to the touch than the dextrins made from cereals or tapioca, which do cling to the hand.

Smell and Flavour.—Most types of dextrin have a characteristic odour, and after a little practice it is possible to distinguish one from another. The odour of dextrin solutions is sometimes very marked, and if a solution cannot be made, a simple test is to moisten the palm of one hand with saliva, place a little dextrin on it, and rub vigorously with a finger until it is quite warm; on cupping the hand over the nose, the characteristic smell of the dextrin is generally quite distinct. The characteristic odour of potato dextrin has been described as resembling that of cucumbers, but the odour of any dextrin is liable to be modified on ageing, the brown varieties of dextrin having the strongest odour, which is somewhat earthy with a faint suggestion of charring. The nearer a dextrin approaches a neutral conversion, i.e. the smaller the amount of acid used as a catalyst, the nearer the smell approaches an 'earthy' odour. By placing and manipulating a small amount of the dextrin on the tip of the tongue, some idea of the acid used in its manufacture, and of the solubility and sugar-content, may be obtained by experienced workers, although the author has found even these to err occasionally.

Moisture Estimation.—The moisture present in a sample may be estimated by direct heating to constant weight in an oven. A temperature of 105° C. for four hours is generally sufficient to drive off all the moisture present in a 5 gm. sample. When a dextrin in liquid form is being examined it is preferable to mix it with a known weight of ignited sand, so that the sand is present in great excess, and then to dry very gently at first, gradually bringing the temperature up to 105° C., at which it is maintained until the loss in weight is constant. While cooling, the hot dish containing the dextrin should be kept in a desiccator over concentrated sulphuric acid, as dry dextrin rapidly absorbs moisture from the air.

It is very difficult to remove all the moisture from dextrin. If a sample of dextrin be taken straight from the roaster, moistened with a known weight of water and then heated to expel this moisture in the usual manner, there is generally a difference of 1 or 2 per cent. between the calculated moisture-content and that found by heating. L. Maquenne has examined this point and records that by drying at 120° C. for one hour, followed by two hours' drying at 100° C. in a current of dried air, the amount of moisture found was 1 per cent. higher than by the usual methods (see p. 335).

From this it may be considered that methods in which the amount of moisture present originally is found by difference are preferable to the method of direct drying. Such methods are quicker to carry out, but the accuracy is limited by the facts that several operations are involved which may result in an accumulative error, and one is dependent on the accuracy of at least two instruments, i.e. the thermometer and the hydrometer.

The method of Brix is a hydrometric one, in which the reading on the hydrometer is multiplied by a factor to give the amount of solid matter taken originally to make the solution. E. Preuss⁹ has modified this method, and dissolves from 4.5 to 20 per cent. of the dextrin in warm water, cools the solution to 17.5° C., and makes the volume up to 100 ml. The specific gravities of solutions of various strengths between the above two concentrations were found to lie between 1.018 and 1.0799, and Preuss gives a table showing the connection between the specific gravity thus found and the moisture-content. For ordinary control or sampling analysis, the method of direct heating is generally employed and sufficiently accurate.

Powdered dextrins usually contain between 8.0 to 14.5 per cent. of moisture, the higher figure being typical of the less converted products. Most yellow dextrins left in contact with

the air in a thin layer for several days take up about 10 per cent. moisture in the first week, and at the end of a further week only an additional 1 to 1.5 per cent. These figures were obtained on one sample of a yellow potato dextrin: it was found that after the first fortnight there was a very slow uptake of moisture, which amounted to only about 0.8 per cent. after six weeks.

Coloration with Iodine.—Practically all dextrins give some coloration with dilute solutions of iodine, ranging from a deep blue, similar to that given by starch and persisting for some time, to a pale reddish-brown that rapidly fades until the solution is colourless. The reaction affords some measure of the degree of conversion, and for factory control, empirical standards applicable to the products of the factory must be drawn up. A small spoon with a round bowl and holding about 0.1 gm. of dextrin is very useful, this amount of dextrin being put into a test-tube of about 20 ml. capacity and containing about 15 ml. of water.¹ To the solution is added N/50 iodine solution in potassium iodide, drop by drop, and after shaking, the colour is examined against that of the standard sample. It must be borne in mind when making this test on dextrin from the roasters that the colour of the solution tends to contain a little more red, which is fugitive, than when the same sample has been re-moistened. It would appear that some sort of oxidation process takes place after the cooling and during the time of re-moistening, which has the effect of slightly altering the colour given with iodine. The number of drops of iodine added, the colour produced, and also the approximate time of fading should be noticed, as all given information concerning the progress of the conversion. The fading of the colour is probably due to the iodine present being reduced by the aldehyde groups of the sugar formed in the roasting, and therefore a very rough idea as to the formation of sugar may be obtained from the rate at which the colour disappears. A 'heavy cooking' white dextrin will give a deep blue coloration with two drops of the solution, and when held to the light will show a deeper blue vertical zone at the centre of the tube. As the conversion proceeds this zone disappears, the blue colour becoming more uniform and darker. The time taken by the colour of both the solution and the deposit to fade is also much quicker, and less deposit is observed.

Some typical results obtained with the iodine solution on dextrin from the roasters are given below:—

'Heavy cooking' white dextrin: 1 drop; deep blue; fades very slowly.

'Medium cooking' white dextrin : 2 drops ; deep blue ; fades more quickly and shows less deposit than above.
 Canary dextrin, medium conversion : 4 drops ; violet ; no deposit.
 Yellow dextrin : 5-6 drops ; red-violet ; fades in about 10-15 minutes.

For factory control O. Saare¹ heats 1 gm. of the dextrin in 5 ml. of water until dissolved, dilutes the solution to 100 ml. with cold water, and adds one drop of N/10 iodine. He notes the coloration produced by the falling drop, after which the tubes are shaken and the colour of the homogeneous solution observed.

Saare's results showing the colours obtained and the amount of soluble dextrans present in various samples are appended :—

TABLE XXVI

<i>Falling Drop</i>		<i>After Shaking</i>	<i>Percentage of Soluble Dextrin</i>
Blue	• • • • •	Blue	• nil
Blue	• • • • •	Pale blue	• 6.1
Blue-violet	• • • • •	Pale blue	• 15.2
Violet	• • • • •	Violet	• 39.2
Violet-red	• • • • •	Pale violet	• 49.5
Reddish-brown	• • • • •	Colourless	• 62.5

It must be borne in mind that in the absence of a rational method of measuring the colour values, the opinion of two different observers on the same colour may vary considerably. The highly converted dextrans that are completely soluble in cold water show very little differences towards N/10 iodine solution, but the use of a N/50 iodine solution allows of a better differentiation, and the rates of fading also give useful indications. With the most highly converted dextrans, however, scarcely any differences are noted and the method ceases to be of value.

Viscosity and Stability.—The determination of the viscosity of the solution made by dissolving a known amount of dextrin in water is extremely valuable in factory control. Such determinations can be carried out in a few minutes. For white dextrans a 50 per cent. solution can be employed, but for well-converted dextrans a 66.6 per cent. or even a 75 per cent. solution can be taken.

The dextrin is taken from the roaster and rapidly weighed, added to a known weight of water, and heated to 80° C. until completely dissolved. It is then cooled to 50° C. and the viscosity determined with a viscometer of the pipette type, i.e. one in which the time for the liquid surface to pass between two marks on the top and bottom tubes, respectively, of a pipette is measured. The pipette is enclosed in a hot-water jacket maintained at 50° C. If

the type of dextrin to be matched contains a known moisture-content, the anhydrous sample from the roaster is weighed out and sufficient water added to ensure the final solution containing 50 or 66.6 per cent. of the re-moistened dextrin. For example, assuming that the dextrin to be matched contains 10 per cent. moisture, 90 gm. of the sample from the roaster is dissolved in 110 gm. water, giving 200 gm. of dextrin solution containing 100 gm. of remoistened dextrin containing 10 per cent. moisture. The viscosity is determined, and if required the conversion continued until the viscosity of a sample determined in this manner is the same, or just a little greater, than that of the sample being matched when the roaster is discharged.

To determine stability, the solution used for the viscosity determination is set aside for 24 hours and then examined to see if any appreciable increase in the viscosity has taken place and if any cloudiness can be observed in the solution made from a yellow dextrin.¹ In yellow dextrins that have been 'burnt,' i.e. have had insufficient acid added as catalyst and have therefore required a higher temperature or longer time for conversion, a distinct cloudiness is often observed which is sometimes so marked as to make the solution look like a yellowish paste. Such dextrins may have the same solubility as the standard and the same viscosity when first made, but this may increase on standing. A good dextrin should show scarcely any appreciable increase in viscosity and have practically the same appearance as when set aside the previous day.

If the solution be kept for several days a large number of fine cracks may appear on the surface, denoting the presence of an excessive amount of sugar which may render the dextrin unsuitable for use in adhesives.

Mineral Matter.—A good dextrin should be free from sand, grit, or any other extraneous matter. A determination of the ash will give an indication of the presence of any excessive amounts of the first two substances, as the ash-content of a dextrin is very close to that of the starch from which it is made (after making allowance for the difference in moisture-content between the two substances). Thus potato dextrins have an ash-content of about 0.5 per cent., maize dextrins about 0.1-0.2 per cent., and tapioca dextrins 0.2-0.6, or even a little more. In each case about 60 per cent. of the ash is soluble in hot water or dilute acid.

For determining ash-content, 10 gm. of the dextrin are incinerated in the muffle furnace at a fairly low temperature, and before the operation is complete the contents of the dish are moistened with one or two drops of ammonium nitrate solution

and re-ignited. Calcium is often present in the ash and also sulphates, chlorides, and phosphates.

Some dextrans met with in commerce are of the prepared type, and contain certain ingredients so that they give an adhesive by mere solution in water. The so-called 'arable gums' are of this type. Such dextrans contain soda ash and sometimes borax, and others contain agents which, by virtue of a bleaching effect, lighten the colour of the solution. One process for attaining this end is to spray the dextrin in the re-moistening plant with a solution of sulphur dioxide and, at a later stage, borax solution or one containing sodium bisulphite or persulphate. The smell and colour of light-coloured dextrans are reduced by this processing, but with dark-coloured dextrans the reduction in the intensity of colour is not worth the extra process; in any case, the colour of the dextrin invariably returns when alkali is added to the solution of a dextrin that has been bleached by reducing agents.

The presence of these extraneous compounds may be suspected from the ash-content, and generally an examination of the ash will give indications of the previous history of the sample.

Acidity.—In making a dextrin by the torrification process, a certain amount of the acid catalyst is lost in the preliminary drying process, and a still further loss occurs in the course of the roasting, whereby in general the higher the temperature of the conversion, the less is the acidity of the finished product.

To determine the acidity, 10 gm. dextrin are dissolved in 100 ml. water and titrated with N/10 caustic soda, using phenolphthalein as indicator (see, however, p. 340). The figure for the titration should not exceed 5 ml. of the soda solution. The following figures were obtained from three samples of tapioca dextrans :—

Lightly converted dextrin : practically neutral.

Moderately converted dextrin : 0.7 ml. N/10 NaOH.

Well-converted dextrin : 1.6 ml. N/10 NaOH.

The first dextrin had little acid added at the start and a high temperature was needed to bring about the required conversion; the second dextrin had more acid and needed a somewhat lower temperature, whilst the third received still more acid, and was converted at a relatively low temperature; thus the time of roasting has some effect on the final acidity factor. Sometimes the acidity may be due to the presence of sulphur dioxide, and according to H. Tryller, it depends largely on the conditions of titration (see p. 340). Little information of practical value is obtained

by determining the acidity, and it certainly gives no indication whether the dextrin has been made by the acid process or not.

Solubility in Cold Water.²—Twenty grams of the dextrin are well shaken with 100 ml. of water and when all the large lumps have been dispersed it is diluted with another 100 ml. of water, shaken for a further 10 minutes, and then rapidly filtered through a dry filter paper. Finally, the density of the filtrate is taken with the Brix hydrometer, the reading of which multiplied by 10 gives the percentage of dextrin soluble in cold water.

The percentage of dextrin soluble in hot water need rarely be determined, as most dextrans are completely soluble.

Determination of Starch in Dextrin.—The solubility and physical behaviour of dextrin may be strongly influenced by the presence of unchanged or soluble starch, so that a method of determining starch is required. M. C. Lamb and A. Harvey¹³ determine the amount of ash and sugar in a cold-water extract of a dextrin and by difference obtain the weight of dextrin. The insoluble matter they return as starch. F. W. Babington, A. Tingle, and C. E. Watson¹⁴ consider that imperfect separation of the dextrin from the starch, slow filtration, and the amount of starch which passes into solution, constitute serious disadvantages of the method. They determine the starch indirectly by precipitating it with a half-saturated solution of barium hydroxide and estimating the dextrin in the filtrate, making allowances for the ash-content of the soluble material.

Caesar and Cushing²¹ have made a series of maize and cassava dextrans, withdrawing samples at intervals and testing them for solubility, alkali-labile value (see p. 344) and the barium hydroxide value by the method of Babington, Tingle and Watson. These values were plotted against time of conversion. The results vary within certain limits and with some products vary linearly with the concentration of barium hydroxide. This tends to show that the barium hydroxide method for determining dextrin is arbitrary. It appears to be primarily an index of the relative size of the amylaceous micelles. These workers suggest that the alkali-labile value curve probably affords the most satisfactory approach to the classification of a starch or a dextrin.

The method of J. J. Chinoy, F. W. Edwards, H. R. Nanji,¹⁵ makes use of the fact that 'starch iodide' is quantitatively precipitated by 95 per cent. alcohol and certain coagulants. F. W. Edwards and co-workers¹⁶ elaborated on this method as follows: One gram of the material is gelatinised with 0.7 per cent. potassium hydroxide solution, cooled and diluted to 200 ml. Ten ml. of this solution are neutralised to phenolphthalein with dilute

acetic acid and 1 ml. of 0.1 N iodine solution is added, followed by 40 ml. of a reagent made by mixing 4 ml. of 10 per cent. potassium acetate solution to a 100 ml. of 50 per cent. (by volume) alcohol. Ten minutes later the supernatant liquor is decanted through a tared alundrum crucible, the residue in the beaker is washed several times by decantation with 50 per cent. alcohol, and twice with 95 per cent. alcohol, transferred to the crucible using more than 95 per cent. alcohol, dried and re-weighed. The washing liquid at each decantation is, of course, poured into the crucible. Using this method, the weight of starch iodide found multiplied by 0.8865 gives the amount of starch present.

Determination of Dextrin in Presence of Starch.—One gram is pasted with 5 ml. of cold water and after adding 100 ml. of hot water the solution is gently boiled for 30 minutes. It is then transferred to a 200 ml. flask, cooled, and made up to 200 ml. with the cold-water washings of the beaker.

Twenty ml. of the solution are transferred to a graduated 100 ml.-graduated flask, 2 ml. of 0.1 N iodine solution added, and the liquid made up to the mark with the potassium acetate/alcohol reagent mentioned above. After shaking the flask and standing for 5 minutes the suspension is filtered. Fifty ml. of the filtrate are evaporated to 3-4 ml., cooled, and the dextrin precipitated by the addition of 100 ml. of 95 per cent. alcohol. After standing overnight the suspension is filtered through a tared crucible of medium size, washed with 95 per cent. alcohol, dried and re-weighed.

Determination of Sugars.—The amount of sugar present in a dextrin may be determined directly, using Fehling's solution with methylene blue as internal indicator. Although some dextrans have a slight reducing action, for general purposes it may be ignored. The sugar found is returned as dextrose, although some of the reducing matter present may be maltose, especially in long 'roasts' or in roasts carried out at high temperatures. The cupric reducing powers of certain dextrans have been determined by G. W. Rolfe³; some of his figures are as follows:—

White potato dextrin : 0.0778.

Medium-white potato dextrin : 0.0342.

Light-canary dextrin : 0.0673.

Well-converted tapioca dextrin : 0.0374.

Fairly well-converted maize dextrin : 0.0802.

This worker found no connection between the cupric reducing power and the specific rotation of 13 commercial samples of

dextrin. O. Philipp²⁰ finds that the amount of dextrose formed depends on the amount of acid used (see p. 112). Rolfe³ considers that a figure greater than 2 per cent. for this value indicates the use of acid as the catalyst, and this the author has confirmed.

One of the most widely adopted methods of estimating sugars is due to Lane and Eynon¹⁷ and is carried out as follows: Add to a known amount of the Fehling's solution (Soxhlet's modification), say 10 or 25 ml. contained in a 400 ml. flask, enough of the solution to reduce nearly all the Fehling's solution and boil gently for two minutes, add one or two drops of a 1 per cent. methylene-blue solution and run in the solution under examination from a burette a few drops at a time; not more than 1 ml. or less than 0.5 ml. should be necessary. The end-point is reached when the boiling solution in the flask goes green and then suddenly changes to orange. With a fresh portion of the solution the determination is repeated until the end-point is reached, a high degree of accuracy being attainable. The strength of the sugar solution should be such that not less than 15 ml. or more than 50 ml. of it is required for the volume of the Fehling's solution used (10 ml. or 25 ml.). The final titration should be carried out as quickly as is compatible with accuracy, and the liquid should be gently boiling all the time to exclude air, which causes the colour of the indicator to return. For this reason the determination is carried out in a flask and not in a dish as directed in some literature. By reference to the tables worked out by Lane and Eynon the amount of sugar present can be found. The accuracy of this method has been checked by H. T. S. Britton and L. Phillips,²² using a potentiometric titration method.

In the Lane and Eynon method the same volume of indicator must be used for standardising the Fehling's solution as is used in the assay and the methylene blue preferably added just before the titration is complete.²³

Another indicator which may be used is that of Ling, which is prepared by dissolving 1.5 gm. ammonium thiocyanate and 1.0 gm. ferrous ammonium sulphate in 10 ml. water at about 40° C., cooling the solution, and adding 5 ml. concentrated hydrochloric acid. Should this solution show a reddish tinge, a little zinc dust may be added to decolorise it. This indicator is used externally. The end-point is reached when no red coloration is produced on mixing the two solutions. The external indicator, however, is not so satisfactory as the methylene-blue indicator. Stieglitz and Horne¹⁸ determine the end-point electrometrically and get results closely agreeing with those given by the above method.

The method of G. M. Kline, S. Slater and S. F. Acree^{4,5} for the determination of aldose sugars may be used to estimate the amount of dextrose in dextrin when the former is present to the extent of 4 per cent. or less, and is stated to be accurate to 0.05 per cent. The method depends upon the fact that alkali added slowly to an aldose sugar solution containing iodine tends to react with the sugar in preference to forming the iodate, which does not appear until the oxidation of sugar is complete. H. S. Miller⁶ has pointed out that ketose sugars are negligibly affected and F. A. Cajori⁷ notes that in this reaction maltose is oxidised more slowly than glucose.

The test is carried out as follows : To 2 gm. dextrin, if necessary previously neutralised with a predetermined amount of alkali in the absence of an indicator, are added 11 ml. N/10 iodine followed drop by drop by 16.5 ml. N/10 NaOH. After two minutes the solution is acidified with N/10 sulphuric or hydrochloric acid and the liberated iodine titrated with N/10 sodium thiosulphate using starch indicator. If the excess iodine does not lie between the limits of 1.5-3.0 ml. of N/10 thiosulphate solution the process is repeated with different quantities of iodine and sodium hydroxide solution, which must, however, always be present in the ratio 2 : 3. The iodine and sodium hydroxide solutions may be added in portions of 4 ml. and 6 ml. respectively, shaking after each addition, and the temperature should be approximately 25° C. For pure dextrose solutions 8 minutes is the best length of time to leave the solution before acidification ; less time than this tends to give incomplete oxidation and a longer time tends to produce over-oxidation.

If the iodine liberated requires more than 3 ml. of 0.1 N thiosulphate solution too much iodine has been added, resulting in over-oxidation, but if less than 1 ml. is required insufficient has been added. After a preliminary trial the amount of iodine solution to be taken for a second time can be estimated by adding 2 ml. to the previous amount used less the number of ml. of thiosulphate solution required.

After titrating the iodine, the excess acid present may be titrated against phenolphthalein, and a figure thus obtained for the amount of sodium hydroxide used in the reaction. This figure should act as a check on the value for the amount of iodine used, as will be seen from the equation :

$R. CHO + I_2 + 3 NaOH = R. COONa + 2 NaI + 2 H_2O.$
Each ml. of 0.1 N iodine solution used represents 0.009 gm. of dextrose.

When adding the alkali the liquid should be well shaken.

The best indication of the end-point is a rapid jump in the amount of iodate present, as a small amount of iodine (detectable with starch) can exist in solution with unoxidised sugar. An iodate-content equivalent to 2 ml. or more of 0.1 N thiosulphate solution shows that the end-point has been reached, whereas a low iodate-content shows that insufficient iodine has been added.

Braun and Bleyer⁸ consider that it is very doubtful whether many dextrans do contain dextrose and that any reducing power shown by solutions of these substances are due to the dextrans themselves; therefore the figures obtained by the usual Fehling's method are quite empirical, whilst those obtained by the above method are stoichiometric in terms of oxidation of the CHO-groups. Actually, the figures obtained by both methods are in close agreement.

H. S. Miller⁶ has shown that lactose is oxidised more slowly than dextrose, and points out that if sodium carbonate is used as the alkali the oxidation of maltose is appreciably slower than that of dextrose. The above method therefore offers a good means of determining the various sugars, sometimes in the presence of one another.

F. W. Edwards and co-workers¹⁶ find that the method of C. L. Hinton and T. Macara¹⁹ gives reliable results. In this method 10 ml. of a 1 per cent. solution of the dextrin are diluted to 50 ml., after which 1 ml. of 0.1 N potassium hydroxide solution, 2 ml. potassium iodide solution (10 per cent.) and 10 ml. of Chloramine T solution (7.1 gm./l.) are added in that order. At the end of 90 minutes the solution is acidified with sulphuric acid and the liberated iodine titrated with 0.02 N sodium thiosulphate. A blank determination should also be carried out without the dextrin. Every ml. of 0.02 N sodium thiosulphate used represents 1.8002 mg. of dextrose or, in the case of dextrans produced with enzymes, 3.148 mg. of maltose.

Detection of Dextrin in Presence of Glue.—Occasionally a dextrin is used to adulterate an animal or fish glue, or it may be added for some particular and more honest purpose. Therefore, a method for its examination and estimation may be briefly noticed. When a glue contains added dextrin the addition may often be detected by a microscopical examination, providing the sample has not been heated too long and the dextrinisation of the starch has not been carried too far. The iodine test may or may not give an indication of the presence of dextrin, depending on the amount of conversion and the colour of the glue, which may mask the reaction if too dark.

J. Alexander¹⁰ has evolved a method which overcomes these

difficulties and allows of the determination of the amount of dextrin added: 0.6 gm. of glue are soaked in 10 ml. of dilute hydrochloric acid (5 pts. of conc. hydrochloric acid to 100 pts. water) and the mixture hydrolysed by heating at 60° C. After hydrolysis the solution is made up to 50 ml., neutralised, and the dextrose estimated with Benedict's solution. The figure obtained for the amount of dextrose present multiplied by 0.9 gives the amount of dextrin present.

Chlorine.—The presence of chlorides or of hypochlorous acid is sometimes observed and for many purposes may be undesirable. The presence of chlorine may be accidental, as when the starch has been insufficiently washed after manufacture, or hypochlorite may have been deliberately added during the re-moistening of the dextrin in order to bleach and reduce the odour. It may be estimated volumetrically in neutral solution, using silver nitrate with potassium chromate as indicator.

Another source of chlorides in dextrin and starch which is, however, rare, is that due to spoilage or contamination with seawater. In the very few cases of this kind that have come to the notice of the author, there were other obvious indications of the source of spoilage, but the presence of abnormally high amounts of chloride in these cases confirmed that contamination had taken place during transport by sea and was not due to rain, wet storage, or transport conditions after landing.

The amount of chlorine found may possibly indicate more or less at what point of manufacture it entered the dextrin, i.e. via the starch, due to insufficient washing, or as a deliberate addition, or as contamination.

REFERENCES

1. O. SAARE, *Zeit. Spiritusind.*, 1900, **23**, 53.
2. F. LIPPMANN, *ibid.*, 1902, **25**, 237, 249, 269, 291, 304, 316.
3. G. W. ROLFE, *Eighth Int. Congr. Appl. Chem.*, 1912, **13**, 237.
4. G. M. KLINE and S. F. ACREE, *Ind. Eng. Chem. (Anal. Ed.)*, 1930, **2**, 413.
5. S. SLATER and S. F. ACREE, *ibid.*, 1930, **2**, 274.
6. H. S. MILLER, *ibid.*, 1937, **9**, 37.
7. F. A. CAJORI, *J. Biol. Chem.*, 1922, **54**, 617.
8. BRAUN and BLEYER, *Zeit. anal. Chem.*, 1929, **76**, 32.
9. E. PREUSS, *Zeit. Spiritusind.*, 1925, **48**, 326.
10. J. ALEXANDER, *Ind. Eng. Chem. (Anal. Ed.)*, 1933, **5**, 200.
11. F. L. P. KRIZKOVSKY, *Mell. Textilber.*, 1925, **9**, 594, 766.
12. W. HÖNSCH, *Chem.-Ztg.*, 1934, **58**, 76.
13. M. C. LAMB and A. HARVEY, *J. Soc. Dyers Col.*, 1918, **34**, 10.
14. F. W. BABINGTON, A. TINGLE, and C. E. WATSON, *J. Soc. Chem. Ind.*, 1918, **37**, 257T.
15. J. J. CHINYOY, F. W. EDWARDS, and H. R. NANJI, *Analyst*, 1934, **59**, 673.
16. F. W. EDWARDS, H. R. NANJI, and W. R. CHANMUGAM, *ibid.*, 1938, **63**, 697.
17. J. H. LANE and L. EYNON, *J. Soc. Chem. Ind.*, 1923, **42**, 32T, 143T, 463T.

- 1925, **44**, 150T; 1927, **46**, 434T; 1931, **50**, 85T; see also J. FITELSON, *J. Assoc. Offic. Agric. Chem.*, 1932, **15**, 624.
18. E. R. STIEGLITZ and L. C. HORNE, *Proc. Queensland Soc. Sugar Tech.*, 1936, 101.
19. C. L. HINTON and T. MACARA, *Analyst*, 1927, **52**, 668.
20. O. PHILIPP, *Zeit. Chem.*, 1867, **10**, 400.
21. G. V. CAESAR and M. I. CUSHING, *Ind. Eng. Chem.*, 1939, **31**, 921.
22. H. T. S. BRITTON and L. PHILLIPS, *Analyst*, 1940, **65**, 18.
23. A. R. LING and W. A. CARTER, *Analyst*, 1930, **55**, 730.

ADDITIONAL REFERENCES

- V. KONN, *Chem. Obzor.*, 1936, **11**, 68. (Estimation of borax in starch preparations.)
- ALLEN, 'Commercial Analysis, Organic,' 5th edit., vol. I, Blakiston, 1923. (Analysis of dextrin.)
- T. ZEREWITINOFF, *Zeit. anal. Chem.*, 1911, **50**, 680. (Methyl magnesium iodide used to determine moisture.)
- J. F. HOFFMANN and J. H. SCHULZE, *Woch. Brau.*, 1903, **20**, 217. (Sample distilled with toluene/turpentine mixture at 150° C. and water condensed and measured.)
- O. KAMM and F. H. TENDICK, *Paper*, 1919, **24**, 1091. (Estimation of dextrin and soluble starch in paper.)
- F. T. VAN DER VOORST, *Chem. Weekbl.*, 1940, **37**, 180, 220. (Determination of sugars in dextrin.)
- A. JONESCU and E. SPIRESCU, *Bull. Soc. Chim. România*, 1924, **6**, 101. (Ferri-cyanide method for determining dextrose.)

CHAPTER 19

PHYSICAL METHODS OF CHARACTERISING STARCH

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THE industrial uses of starch are so numerous and the requirements of the product are so varied that a large number of techniques are necessary for its complete characterisation. The problems encountered are further complicated because of the many varieties of starch which are important in industry and the numerous modifications produced by oxidation, acid modification, dextrinisation, and other methods. Some tests are made by the starch manufacturer to control the quality of his products during processing or to ensure that they meet required specifications. The same or other tests may be made by the consumer to check the specifications or to compare competitive products. Still other investigative methods are used in research on fundamental problems of starch chemistry or in the development of new or improved products.

In the consideration of the problem of investigating starch it is important to note that the literature on the subject contains almost innumerable references to instruments and techniques for the purpose, of which some are only of historical interest at present. It would be impossible to consider all of them, and in this chapter attention will be centred on those of importance at the present time, and especially on those which have proved valuable in the industrial evaluation of starch products. It occasionally happens that methods which are reported in the literature have not proved of general value for this purpose, and on the other hand some methods of great value in industry have not been published and are therefore not widely known.

Starch products find their greatest use in the textile, paper, adhesive and food industries. They are usually cooked with water and used as hot or cold fluids or as gels. It is customary to refer to dispersions of cooked starch in water which are fluids as starch pastes, and this term is used to indicate even those which are very

dilute and which do not seem pasty at all.¹ While in many theoretical studies quite dilute pastes are often used in order to avoid complicating effects which occur at higher concentrations, many of the industrial tests must be made on pastes of a great enough concentration so that the properties determined permit an adequate prediction to be made of the industrial performance of the product. The number of tests required and their nature depend on the purpose of the examination and the circumstances under which it is made. They will be enumerated and classified below and the description of the individual tests will be given later in the chapter.

It is apparent that the starch manufacturer, knowing the variety of starch and the treatment to which it has been subjected, need only make a limited number of tests when the purpose is quality control and standardisation of the product. Those usually made are :

- (a) Viscosity or fluidity of hot starch paste. (b) Alkali fluidity, especially for acid modified starches. (c) Colour. (d) Odour. (e) Hydrogen ion activity or *pH*. (f) Acidity or alkalinity. (g) Moisture.

In addition, some supplementary tests are made of starches intended for certain uses. These include :

a. Cold paste viscosity if the starch is to be used cold as in the case of certain adhesives ; or at relatively low temperature, 120° to 135° F., for paper coating.

b. Gel properties if it is intended for use as a gel or in products such as salad dressing, pudding, and some candies where its use depends on its gelling tendency in combination with other materials.

c. Foreign matter.

d. Bacterial tests if it is to be used in food.

e. Flow properties or mobility if it is to be used for certain purposes such as a dusting powder for rubber where a highly mobile product is necessary, or in condiments where it is often used with the ground materials to cause them to sift easily. On the other hand there are uses for which a mobile starch is unsuited. An example is its use in pharmaceutical tablets such as aspirin where a mobile starch will not form a firm, strong tablet.

For the examination of an unknown starch or for the comparison of competing starches some of the following tests must usually be made in addition to those listed above :

a. Microscopic examination.

b. Analysis for mineral matter. This may be simply a deter-

mination of total ash, or a qualitative or quantitative analysis may be required.

c. Analysis for nitrogen. This may be necessary to determine the presence of added nitrogenous matter.

d. Analysis for fat, to determine whether fats, oils, soaps, or similar products may have been added.

e. Determination of water soluble material, which may show the extent of modification of the starch or the presence of added substances.

f. Examination of opacity of the paste, which is of assistance in determining the variety of starch.

g. Determination of the gelatinisation range, which is of value in establishing the variety of starch and the treatment it has been given.

All of the methods given above are also useful in theoretical research or in the development of new or improved products, and in addition numerous other techniques may be employed. Important among these are :

a. Alkali lability number.²⁻⁴

b. Copper reducing number.^{5,6}

c. Iodine titration.^{7,8}

d. Fractionation of starch by complex formation.^{9, 10}

e. Action of enzymes.¹¹

It is the function of this chapter to present only the physical methods of testing starch. Tests of a chemical nature will be discussed elsewhere (see Chap. 13).

Viscosity.—The most important of all industrial tests used to characterise starches is that of paste viscosity. It is generally recognised that to obtain a measure of the true viscosity of a hot starch paste it must be determined at very low concentration.¹² At higher concentrations pastes deviate from true Newtonian properties of viscous flow.¹³ While much research has been done on very dilute pastes, examinations made for industrial purposes must be made on those which are more concentrated and which have anomalous viscosity. Such terms as 'viscosity,' apparent viscosity, and consistency have been proposed¹⁴ for this property. However, within the starch industry it is generally referred to simply as viscosity and this term will be used in this chapter to correspond to general usage.

The anomalous viscosity of starch pastes has been investigated by Farrow and co-workers,^{18,19} Alsberg,²⁰ Galloway,^{21,22} Katz,²³ Brimhall and Hixon,¹² Taylor and Beckmann,²⁴ Schoch²⁵ and others. These studies show that the properties of pastes of un-

modified starches, even after considerable cooking, are not primarily colloidal phenomena but are due to the presence of larger aggregates including undisintegrated granules. The work of McDowell and Usher²⁶ indicates that the swollen granules form a structure which encloses portions of the liquid phase, thus increasing the viscosity. The presence of such structural viscosity can be demonstrated by making a viscosity determination of a hot paste of unmodified corn starch immediately after agitating it. A second test made after the paste has stood a short time without agitation will show an increase in viscosity.

For the determination of starch viscosity any good viscometer can be used, and an examination of the literature shows that practically all have been, by one investigator or another. A review of some of the methods has been given by Blinc and Samec,²⁷ while excellent discussions of viscometers and the problems of viscometry are given by Barr,¹⁵ Hatschek,²⁸ and Bingham.²⁹

Because the observed viscosity of starch depends on the technique employed in preparing the paste and in making the test,³¹ the entire procedure must be standardised with the greatest care in order to obtain satisfactory results. To be specific, the factors which must be controlled with precision are given below. (a) The initial temperature of the water used for the paste should not vary greatly. (b) The rate of increase of temperature must be the same in all tests. (c) The highest temperature to which the paste is cooked should be closely controlled, and should not vary by more than a few tenths degree Centigrade. (d) The rate of stirring must be uniform. (e) The type of stirring and the dimensions of the stirrer must be accurately duplicated. It is essential that the entire quantity of paste be heated uniformly. This requires that the paste which forms on the sides and bottom be stirred into the main body of material. If this is not done an insulating layer forms on the walls of the vessel and retards the cooking of the remainder. (f) It is necessary that the time of cooking and the total elapsed time from the beginning of the cooking process until the viscosity test is started be closely duplicated. (g) Evaporation of water from the paste must be kept uniform and should be minimised by use of a close-fitting cover with a condenser. (h) Differences in pH produce changes in viscosity^{32, 36, 119} which must be considered in testing. (i) Extraneous materials of many kinds both organic and inorganic including salts, acids, alkalis,^{32-35, 37, 38} fats,³² and proteins,³⁶ affect viscosity. This, of course, includes minerals which may be found in natural waters.

It follows that for viscosity tests the paste should be made with

distilled water, it should be cooked in a water bath which is thermostatically controlled, stirring should be done mechanically, and the stirrer should be powered by a motor which will maintain constant speed under varying load. Furthermore, when the paste is transferred to the viscometer it is necessary to perform this operation quickly to minimise the drop in temperature which will occur. The viscometer must be preheated to the temperature of the test to avoid heat loss from the paste to the instrument, and great care must be exercised to ensure that it is clean.

Orifice Flow. The commonest method used for the industrial determination of starch viscosity is the measurement of the rate of flow of a definite volume of paste through an orifice. In some cases the time in seconds required for a definite volume to flow is measured, and this is taken as the relative viscosity without changing it into absolute viscosity units. In other cases the volume which flows in a definite time is measured. This is called the fluidity of the paste. It will be seen that these quantities are the inverse of each other, so that a starch of low viscosity has a high fluidity.

Among the instruments used are the Scott,^{39, 42} Engler,^{41, 42} Saybolt,^{40, 42} and Redfield^{42, 44} viscometers. The Scott appears to be the most widely used industrially, and although there are many techniques^{43, 74} employed for using this instrument, one typical procedure will be described here. This description is given in considerable detail as an example of the care that must be taken to standardise the technique of cooking and testing by any method, and is applicable to other instruments than the Scott.

Scott Test. Weigh the starch accurately on an analytical balance, transfer it to a German silver beaker of 600 ml. capacity and add 280 ml. of distilled water at room temperature. Stir the mixture to suspend the starch, then place the beaker in a rapidly boiling water bath of large size and maintain it at the boiling point during the cooking. Start a stopwatch at the moment the beaker is placed in the water bath and stir the paste vigorously for exactly five minutes. Then cover the beaker with a watch glass and allow it to cook for five minutes without stirring. Next remove the cover, allow the condensate to drain into the paste and stir it for 15 seconds. Replace the cover and continue cooking until 14 min. 45 sec. total cooking time. Remove the cover, drain as before, and stir it for 15 seconds. Rates of stirring in different laboratories vary from 120 to 250 r.p.m. Whatever rate is used must be accurately reproduced in all tests.

While the paste is cooking, heat the Scott cup in its water bath which contains also a conical flask of 250 ml. capacity gradu-

ated at 200 ml. At the end of the 15-minute cooking period quickly measure 200 ml. of paste in the flask and pour it immediately into the Scott cup. Release the plunger at once and at the same time start a stopwatch. The time for a definite volume of paste to flow is known as the Scott viscosity.

Because of the great range of viscosity of starches, the weight of starch used and the volume of flow which is timed vary, depending on the variety of starch and its modification. The same volume of water is used for all tests. For thick starches such as tapioca 10 grams may be used, for unmodified corn starch 15 grams; for moderately thin-boiling starches 28.5 grams, and for those of greatest modification 100 grams. The flow of either 50 or 100 ml. of paste is timed, the volume being chosen so that the time is adequate for accurate measurement and yet is not unduly long. The rate of shear decreases during the test. Therefore the head of liquid in the Scott cup should not be allowed to become low, and volumes greater than 100 ml. are not timed. In order to obtain uniform cooking conditions it is necessary that the liquid level in the water bath be maintained constant. Care must be taken to prevent paste being stirred onto the beaker above the paste level. If a ridge forms, it may harden and such material transferred to the viscometer cup may partly or completely plug the orifice.

In an effort to overcome variations in cooking procedure some laboratories now use motor-driven stirrers. Direct introduction of steam into the paste for heating and stirring has been applied.⁴⁵ This simulates the cooking method employed by many starch users. It requires careful adjustment of steam to produce a uniform rate of heating the starch and a constant rate of boiling. The Scott cup is frequently provided with an overflow at the 200 ml. mark so that the paste can be introduced quickly without first measuring it in another vessel.

Knife-edge Orifice. Another type of orifice viscometer frequently used for both starches and dextrans is one which employs as an orifice a small hole in a thin plate of metal. This is known as a knife-edge orifice. An instrument of this type has been developed at the Penick & Ford laboratory for control and sales service testing. It consists of a metal plate 0.8 mm. thick through which the orifice is drilled, a glass cylinder of 33 mm. inside diameter and 305 mm. length with a section marked by two etched lines to contain 100 ml. The lower of these lines is 120 mm. from the bottom of the tube. The glass tube is connected to the metal plate by means of a simple frame, with a rubber gasket to prevent leakage. For various ranges of viscosity, tubes with orifices of



FIG. 19:1.—A simple Scott Viscometer showing water bath, cup and cover with plunger.

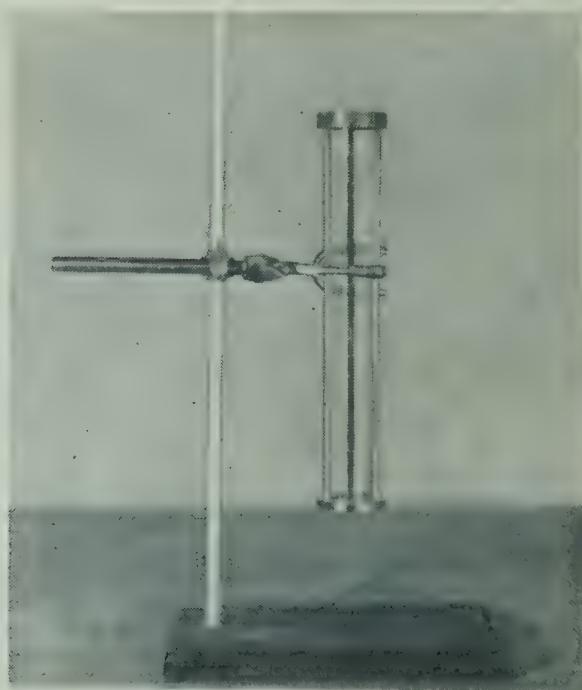


FIG. 19:2.—Penick and Ford knife-edge Viscometer.

1, 2, and 3.5 mm. diameter are used. The apparatus may be enclosed in a constant temperature water bath. Each instrument is standardised by comparison with a master instrument which is kept for this purpose. The cooked paste is poured into the tube until it is filled above the upper etched line, and the time of flow of the paste contained between the lines is noted. This instrument has proved excellent for rapid testing.

Correction for Moisture. Commercial starches contain varying amounts of moisture depending on the source and the conditions in drying and storing them. This will affect the viscosity, for if a standard weight of starch is used in testing, the greater the moisture-content the lower will be the weight of dry starch it contains. For this reason a correction is often made for moisture. This may be done by first determining the moisture in the starch and weighing amounts which will contain the same quantity of dry substance. Where viscosity tests are made frequently on a routine basis a correction chart is usually made on which the viscosity on a dry basis is graphed against viscosity at various moisture levels. The advantages are that the viscosity test may be made without waiting for the results of the moisture analysis, and the routine worker will always weigh the same amount of starch.

Pipettes. Where a rapid approximate determination is to be made on a paste of rather low viscosity, the Dudley⁴⁷ or other pipette is often used. The paste is drawn into the pipette and the flow of the measured volume is timed. The pipette may be equipped with a constant-temperature jacket as in the case of the pipette used by Chrzaszcz and Piorozek.⁵¹ In industrial testing, pipettes are often used without any means of maintaining a constant temperature. Such determinations are subject to considerable error but have the advantage of greater speed and convenience.

Standardising Orifice and Pipette Viscometers. A frequently used method of standardising or comparing orifice and pipette viscometers is to determine the time of flow of a definite volume of water at some chosen temperature. It has been shown by Buel⁴⁶ and by Balderston⁴⁷ that this method is inadequate. One reason is that the water time is often very low so that errors in measuring time will be relatively high. Another reason of great significance is that the relationship between time of flow and viscosity for this type of instrument is given by the formula $n/p = At - B/t$ where n is viscosity, p is density, t is time of flow and A and B are instrument constants.^{16, 30, 48} It is obvious that it is not possible to evaluate the two constants by means of a single deter-

mination. At least two determinations must be made using materials which differ considerably in viscosity, and which preferably lie in the range of those to be tested. Errors are minimised where an instrument is made according to rigid specifications of orifice diameter and length, as is the case with the Redwood, Engler and Saybolt. They are serious where viscometers are made of a funnel with a glass orifice⁴⁹ such as are often used for the alkali fluidity test, and with pipettes,^{47, 50} for it is practically impossible to draw out a number of glass orifices which will be alike.

Capillary Viscometers. Many investigators have used capillary viscometers for starch research. With dilute pastes capillaries without applied pressure have been used,²⁷ while with more concentrated pastes pressure is applied, as by Richardson and Waite³² and Brimhall and Hixon.¹² The use of applied pressure has proved advantageous for studying starch at various rates of shear. Capillary viscometers are not used very frequently for industrial examination of starch because of the greater convenience and ruggedness of other types. They have proved to be excellent research tools.

Rotational Viscometers. Commercial viscometers of the rotational type are widely used for determinations of starch viscosity, though not as frequently as orifice viscometers. They are often used for testing commercial products which contain starch and are especially useful when it is desired to study viscosity at several rates of shear.

Stormer Viscometer. This instrument consists of a rotating cylinder within a sample cup which is surrounded by a small water bath. The cylinder is rotated by means of a falling weight, and an indicator shows the number of revolutions made by the cylinder. In the usual procedure the time for 100 revolutions is taken as the Stormer viscosity, using a weight which will enable the test to be made in a reasonable time. It was used by Rask and Alsberg,⁵² Glarum,⁵³ MacMasters and Hilbert⁵⁴ and others. Geddes and Dawson have derived an equation for transforming Stormer times into absolute viscosity units.⁵⁵ More recently Fischer and Lindsley have modified the Stormer viscometer to make it suitable for measurements in absolute viscosity units,¹²³ and have applied it to the rheological study of starch.¹²⁴ Their work shows that starch pastes are pseudoplastic, for the curves of torque *v.* rate of shear have no linearity, and no intercept on the torque axis corresponding to a yield value.

In a typical routine industrial procedure from 7 to 15 grams of starch, depending on the degree of modification, is dispersed in 100 ml. of distilled water. The slurry is placed in a boiling

water bath and stirred until it reaches 90°C . It is then covered and is allowed to cook undisturbed until 30 minutes after heating was begun. The water bath on the viscometer has meanwhile been heated. The sample is poured into the Stormer cup and the weight is released. The cylinder is allowed to make 10 to 15 revolutions in order to avoid the error due to inertia when it is started, and the next 100 revolutions are timed. Another procedure is described in detail by Barham.⁷⁴ Searle's viscometer⁵⁶ is very similar in principle to the Stormer and can be used equally well.

*MacMichael Viscometer.*⁵⁷ Gallay and Bell²¹ reported the use of this viscometer in their studies of starch viscosity. A critical study of the instrument has been made by Herschel.^{58, 59} It is used regularly in the food industries for flour,⁶⁰ as well as for prepared products which contain starch, such as puddings and salad dressings. In the paper industry it is often used for studying the properties of paper coatings.^{125, 126} It has a sample cup surrounded by a small water bath. Suspended centrally in the cup by means of a torsion wire is a disc. The cup is rotated at constant speed by an electric motor and the twist imparted to the wire is measured in arbitrary units by means of a pointer and dial. There are several interchangeable wires of different sizes so that a wide range of viscosities can be covered. The speed of rotation can be changed readily so that it is possible to study a sample at various rates of shear. This is especially useful in the study of thixotropy, dilatency, and plasticity, as in the preparation of paper coatings.

When used with hot starch pastes two difficulties appear. One is that with thick starch pastes the wire does not reach an equilibrium rapidly. Instead the reading slowly decreases over a period of several minutes due to breakdown of paste structure. In tests with 5 per cent. unmodified corn starch Bechtel found that the reading fell 16 units over a period of 6 minutes. This makes it difficult to decide what reading to take as the viscosity and makes any figure purely arbitrary. The other difficulty is that the water bath, like that of the Stormer, is very small. Even by use of the supplementary heater provided, it is difficult to control paste temperature accurately because of loss of heat to the rather massive disc and the supporting column which surrounds the torsion wire.

Brookfield Viscometer. Another rotational instrument of somewhat different principle is the Brookfield viscometer.⁶¹ It consists of a spindle which is turned at constant speed by an electric motor. Viscosity is indicated by a pointer on a dial and it is very

simple to express the results in absolute viscosity units. There are several easily interchangeable spindles so that it can be used over a wide range of viscosities. One model permits operation at several speeds so that it can be used to determine the effect of different rates of shear. It may be held in the hand during a test, and a guard is provided so that it will be centred in a 600 ml. beaker.

From the foregoing it will be seen that it has many of the same advantages and disadvantages as the MacMichael when used for hot starch paste determinations. One advantage is that it can be used without the necessity of transferring the paste to a special viscometer cup with the resulting lowering of temperature and loss of time. However, it is observed that during tests with this instrument the temperature of the paste slowly falls, due to the large surface exposed to the air. As in the case of the MacMichael, continued rotation of the spindle in a thick boiling starch brings about a steady fall in the reading, making it difficult to select a value for the viscosity of the paste. Its greatest use with starch is in the evaluation of comparatively cool mixtures of starch and other materials, such as paper coatings.

Falling Sphere Viscometer. The falling sphere viscometer has been applied to the testing of starch products. An excellent discussion of the theory of this method and the possible errors and their correction has been given by Barr.¹⁷ The instrument required according to theory must use a sphere of small diameter compared to that of the fall tube. Such a viscometer was used by Gibson and Jacobs.⁶² One possible error is due to the fact that the falling sphere may tend to wander from a straight path.⁶³ A difficulty in applying this instrument to starch pastes is that many pastes, such as those of cereal starches, are rather opaque and it is difficult to observe and time the fall of the sphere. Höppler⁶⁴ developed a relative viscometer using the falling sphere principle in which these difficulties have been overcome. It has been described by Wobser and Müller.⁶⁵ In this instrument a glass fall tube of about 1.6 cm. diameter and 20 c.m. length is enclosed in a water bath equipped with a means for maintaining constant temperature. The fall tube is inclined at an angle of 10° from vertical. It has a series of spheres of varying diameter and material to cover a wide range of viscosities. The inclined tube acts as a guide, causing the sphere to follow a straight path. The spheres are only slightly smaller than the diameter of the tube so that they can be observed easily in starch pastes. However, this type of instrument is very sensitive to structural viscosity of the pastes, as reported by Morgan and Vaughn.⁴⁹

so that its application would seem to be limited either to very dilute pastes or to those of highly modified starches. It has in fact been used for the purpose of determining structure in pastes by Komm and Martin⁶⁶ who measured the time of fall in pastes of starches and dextrans at various intervals of time and extrapolated to zero time. The time of fall at zero time was called labile structural viscosity. The time of fall was found to increase with each passage to a final value which they called the stable structural viscosity.

In this laboratory it has been found by Bechtel that a falling sphere viscometer of theoretical design gives erratic results with thick starch pastes, that with the Höppler type the time of fall in 5 per cent. pastes of unmodified corn starch increases with successive passages of the ball if the recommended 3 minutes is allowed to elapse between passages, and that results with different cooks of the same starch do not agree well. To obtain agreement it was necessary to pass the ball through the paste several times without allowing time between passages, before timing a fall. This makes the method a slow one.

Cold Paste Viscosity.—One cannot derive the viscosity of a cold paste from the hot paste viscosity determination. Starches from different sources and those given different treatment in manufacture differ widely in the extent to which their pastes thicken on cooling. While unmodified tapioca, potato and waxy maize starches have high hot paste viscosities, their cold pastes thicken or 'set back' much less than those of the common cereal starches. When a cereal starch such as corn starch is modified by acid to a moderate extent, the tendency of the cold paste to congeal is much greater than would be expected from its hot paste viscosity. On the other hand, when such a starch is oxidised by hypochlorite, the tendency of the cold paste to thicken is much reduced. Therefore, whenever a starch is to be used in the form of a cold paste, it is necessary to determine the paste viscosity under approximately the conditions of temperature and concentration at which it will be used.

For the determination of cold paste viscosity orifice or capillary viscometers can be used if the concentration of starch is low, for example in the order of 2 per cent. or less for unmodified corn starch, or if the starch is highly modified so that the cold paste is thin. Katz,¹ with 1 per cent. corn and potato starch, used an Ostwald viscometer. Where it is necessary to test pastes of higher concentration and of low degree of modification so that the cold pastes are rather thick, they tend to clog the orifice. In such cases a rotational instrument such as the Stormer or

MacMichael can be used to advantage. The paste should be prepared with all the precautions required for a hot paste, and in the concentration range in which results will be significant in terms of the intended use of the starch. When the paste has been cooked it is placed in a constant-temperature bath to cool to the temperature desired for testing. The cooling period may be about 3 hours, but whatever time is allowed, must be kept uniform so that all pastes will cool at the same rate and to the same temperature. If a skin forms on the surface it must be removed prior to testing.

Since the extent of viscosity increase depends on the time that the paste stands, it is frequently necessary to make further tests after longer periods of time. In commercial practice two tests are often made, one after 3 hours and one after 24. From these data reasonably accurate information is gained about the rate and extent of thickening. It should be observed that the above procedure refers to fluid pastes. If a gel has formed on cooling, it is necessary to use a lower starch concentration.

Viscosity Curves.—The viscosity of a paste changes continuously with heating and stirring. When starch gelatinises the viscosity begins to increase with the swelling of the granules and this continues until a maximum is reached, after which it decreases more or less depending on the variety of starch and the modification it has been given during manufacture. The instruments and methods previously described are best suited for making single determinations of paste viscosity. They have been used to make a number of determinations from which a viscosity curve has been derived, but the process is rather laborious because of the necessity of cooking large samples, and of cleaning the viscometer between tests.

In recent years instruments of a new kind have been developed by which a series of viscosity determinations on a paste can be made readily, or the viscosity curve can be recorded on a chart. Such instruments are of great value because they completely characterise a starch and give the temperature of initial viscosity rise, gelatinisation range, maximum viscosity, time of cooking and temperature at the maximum, and the viscosity at any time during the cooking period, from which the rate and extent of decrease in viscosity after the maximum can be obtained. When it is desired, a cooling curve can also be made.

Another advantage of these instruments is that the entire cooking and testing procedure can be controlled automatically so that the results are entirely free from the effects of variations in technique due to different operators. The value and import-

ance of this feature is made apparent by reference to the detailed cooking and testing procedure given under the Scott Test, in which a slight deviation from the described technique alters the result of the test.

The consistometer of Caesar^{67, 68} has a beaker for the paste, surrounded by an electrically heated water bath. The paste is stirred by a streamlined agitator driven by a constant-speed electric motor, and the changes in viscosity are followed by observing the power input in watts required to drive the agitator through the paste at uniform speed. These readings are then graphed against paste temperature. By passing a stream of cooling water through the water bath the changes in viscosity during cooling can be observed. Its function is to measure viscous and plastic effects in concentrated pastes, with a working range of 15 to 30 per cent. concentration of starches. Caesar has stated that the lower limit of concentration which can be used is 10 per cent.

In their study of the gelatinisation of starch, Mullen and Pacsu¹¹⁶ developed a consistometer of the same principles but somewhat different design. Radley⁶⁹ has designed a similar instrument, only that the power input into the motor is maintained constant and the speed of the stirrer is allowed to vary. In this case motor speed is graphed against paste temperature. The curves are the inverse of those obtained by Caesar. A recording viscometer designed for concentrated pastes by Bauer has been described by Glabe.⁷⁰ It measures the torque against two paddles which are driven at constant speed, and the results are graphed by means of a recording dynamometer. Houtz⁷¹ reported the use of a consistometer similar in principle to Caesar's, in which the power input required to drive a stirrer through the paste is measured.

Barham, Wagoner and Reed⁷² have designed a continuous reading concentric cylinder viscometer for starch. The outer cylinder is driven at constant speed in an electrically heated oil bath. The torque on both internal and external walls of the inner cylinder is measured by adjusting weights on a balance beam until the resistance of the paste is equalled. This instrument is sensitive in a much lower range of viscosities than those previously described. It has been designed for pastes of between 5 and 10 per cent. concentration. They have recently applied their instrument to the study of potato, sweet potato and sorghum starch.^{73, 74} From the results of many tests they find that their precision is within plus or minus 2 per cent.

Recently Higginbotham¹¹⁷ has developed a consistometer for continuous measurement of starch viscosity, and has applied it to problems arising in the evaluation of starches for use in the textile

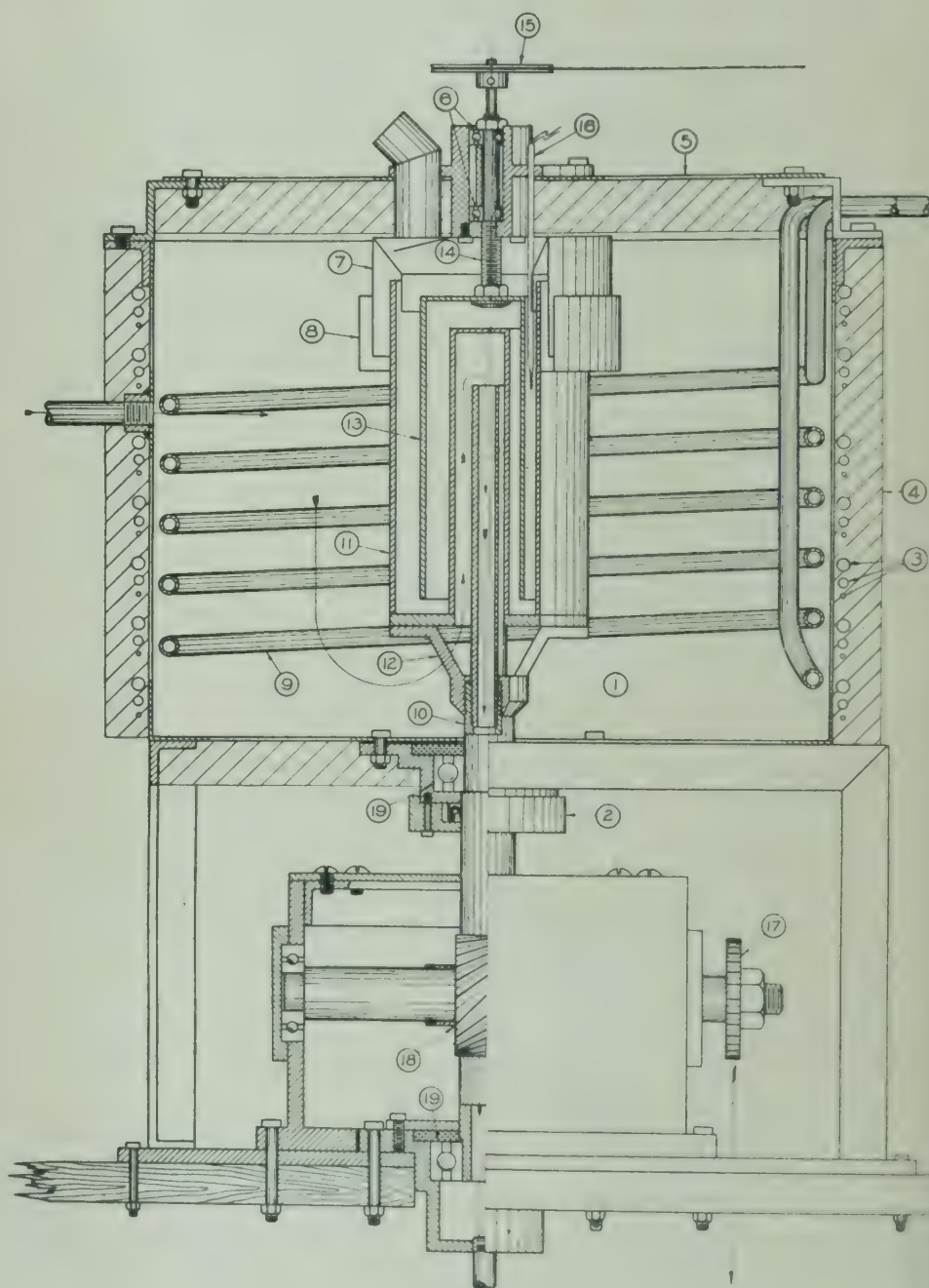


FIG. 19 : 3.—Barham, Wagoner and Reed Viscometer. (1) Oil bath. (3) Electric heaters. (9) Cooling coil. (11) Rotating solution cup. (13) Suspended torque cylinder.

(By courtesy of H. N. Barham)

industry. It is sufficiently sensitive for testing concentrations as low as 5 per cent. of unmodified starches and results have been found reproducible within 1 per cent. A paddle is driven at constant speed through a sample of 170 ml. and the torque against the paddle is transmitted through a differential to a quadrant balance. Readings may be made at any time by means of a pointer and scale. In order to reproduce industrial conditions of preparing sizing pastes, they are usually cooked at 99° C.

The V. I. Viscosigraph of Selling and Lamoen¹²² employs a stirrer driven by a synchronous motor in a housing which rotates on a ball bearing. Attached to the motor housing is a coil spring. When the stirrer operates in a starch paste the torque against it causes the motor housing to rotate until the torque is balanced by the spring. The coil spring is calibrated in gram-centimetres and results are graphed by means of a recorder.

Brabender Amylograph. A widely used instrument of this type is the Brabender Amylograph which is available commercially. It has been described by Brabender,⁷⁵ and by Müller.⁷⁶ The vessel in which the starch is pasted is rotated at a constant speed of 75 r.p.m. in an electrically heated air bath by means of a synchronous motor. The cover, which does not touch the rotating vessel, has several small cylindrical rods which extend down into the paste. It is fastened to a vertical shaft which is connected to a coiled torsion spring. The rods stir the paste when the vessel is rotated, and the torque of the paste against them turns the shaft until it is balanced by the torsion spring. Attached to the spring is a pen by means of which the changes in viscosity of the paste are recorded on a chart of the strip type. An interesting feature is a means for controlling the temperature rise so that it occurs at the constant rate of about 1.5° C. per minute. The thermoregulator can be pre-set so that at any desired temperature no further rise will occur. A recent improvement is a means for controlling the rate of cooling so that it too can be made constant. Anker and Geddes³⁶ have made a critical evaluation of the instrument. They found that duplicate curves agree closely both in the temperature at which significant changes occur and in the values of viscosity. They tested the effect of adding wheat gluten, buffers, enzymes, and cold gelatinising agents. They also showed results obtained with a series of modified corn starches. Meiss, Treadway and Smith⁶¹ used this instrument for measurements with potato starch and studied the effects of drying methods and of water soluble materials.

Corn Industries Viscometer. This viscometer, developed under a fellowship of the Corn Industries Research Foundation, has been

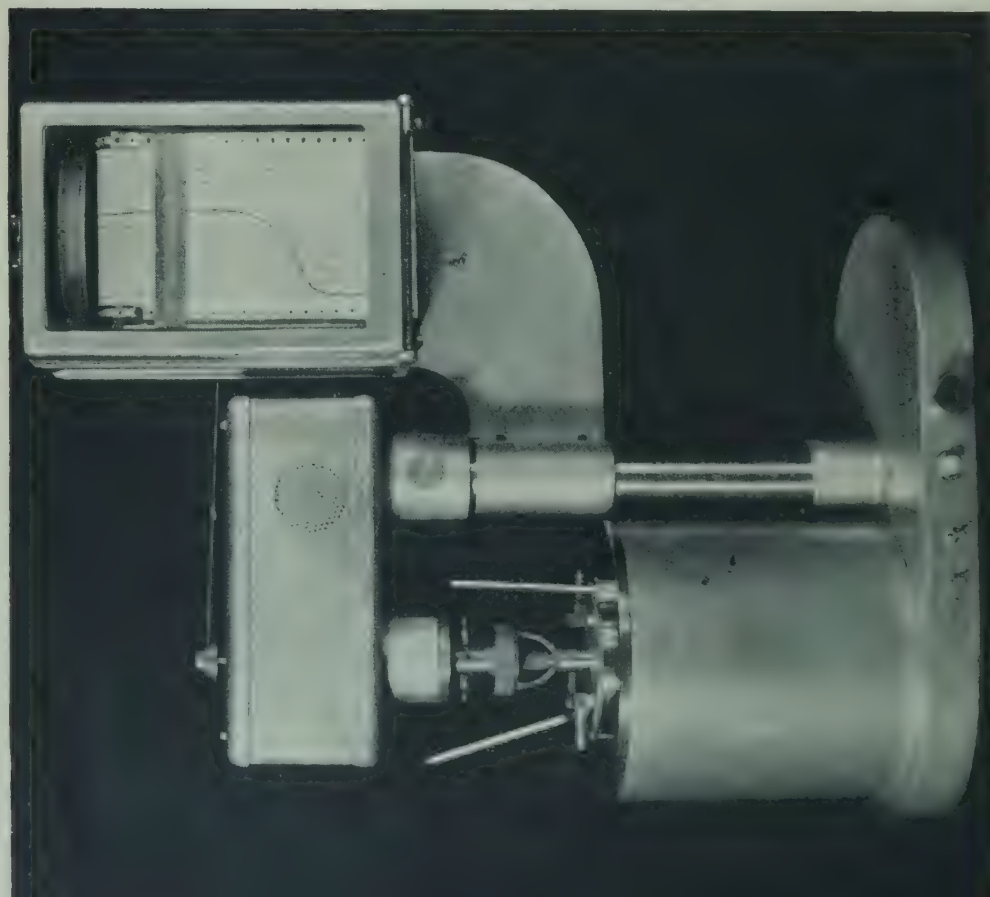


Fig. 19 : 4.—The Corn Industries Viscometer.

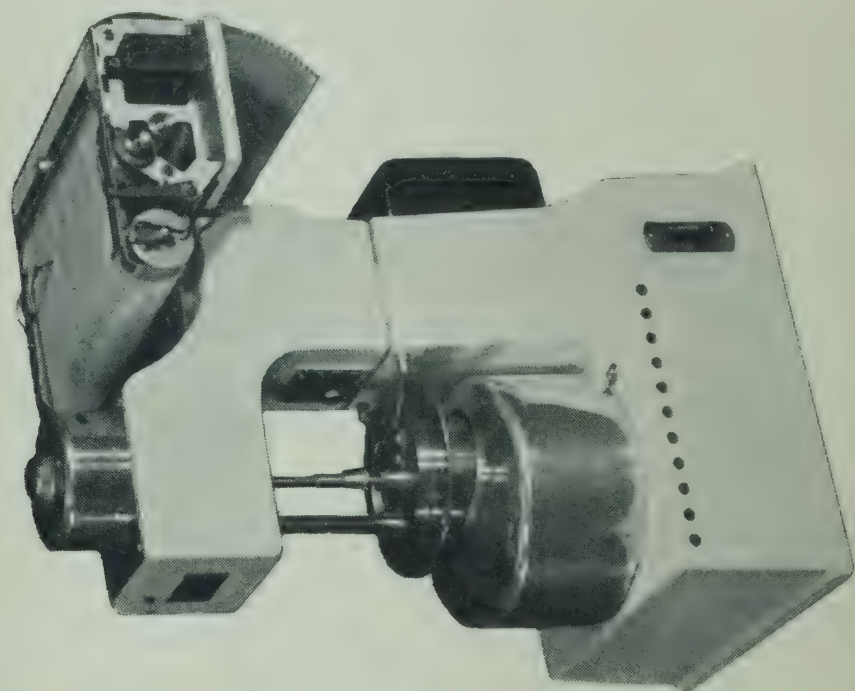


Fig. 19 : 5.—The Brabender Viscograph-Amylograph.
(By courtesy of the Brabender Corp.)

described by Kesler and Bechtel.¹¹⁸ It is being manufactured commercially and is available for general use. The purpose was to design a continuous automatic recording viscometer suitable for general industrial testing in the range of concentrations from 5 to 10 per cent. of unmodified starch. The viscometer has been patented¹²⁷ and has been adopted as the official testing instrument of the corn starch industry of the U.S.A. It has been used by Bechtel and Fischer¹²⁸ for the study of the flow properties of starch pastes.

Starch, suspended in water, is heated in a metal beaker equipped with a close fitting cover and condenser which prevents loss of water by evaporation. Heat is supplied by an electrically heated, thermostatically controlled water bath. Provision has been made for circulating cold water through the water bath so that viscosity may be measured during cooling of the paste.

For any viscosity test the starch must be stirred before it gelatinises, to prevent lumping. After gelatinisation begins stirring should be of such a nature that the entire quantity of paste is cooked uniformly at the same temperature. The importance of adequate stirring is readily apparent, since the viscosity depends on the temperature to which the starch is cooked as well as the time that it is maintained there. Uniform cooking is not easy to accomplish, for convection currents cease in all but the most dilute pastes, and the starch thickens on the walls of the vessel to form an insulating layer which, if it is not efficiently removed, results in rather large differences in temperature between the paste at the walls and that at the centre. Proper stirring is accomplished in this viscometer by use of a mechanical stirrer consisting of two parts, one of which scrapes the wall and bottom of the beaker to remove the adhering layer. The scraper is turned directly by a synchronous motor. Through the hollow shaft of the scraper is a shaft on which is a four-bladed propeller. The propeller has the double function of stirring the body of the paste and of providing the means of measuring viscosity. Power is transmitted to it through a differential. The resistance which the propeller encounters is transmitted by means of this differential to a dynamometer which actuated the pen of the recorder.

To balance the torque a pendulum balance is used. Sensitivity over the wide range of viscosities covered by starches is achieved by use of a series of easily interchangeable weights. This method has advantages over the use of torsion wires because of the ease of changing weights and because they can be interchanged without requiring re-standardisation of the viscometer.

Application has been made to the study of a number of starch

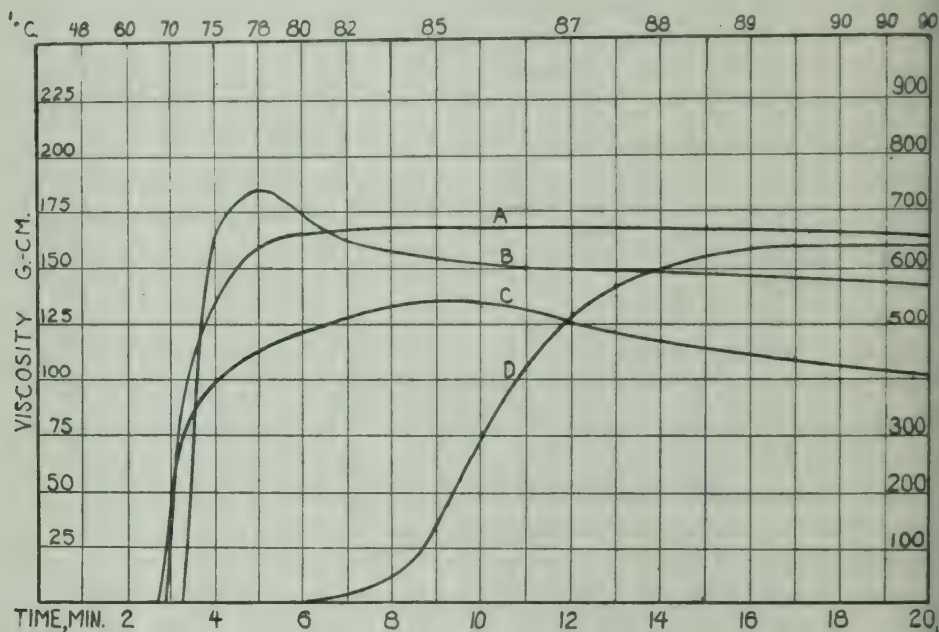


FIG. 19 : 6.—Corn Industries viscometer curves of 5% starch pastes. (A) Potato. (B) Waxy Maize. (C) Tapioca. (D) Corn. Viscosity scale for (A) and (C) at right ; for (B) and (D) at left.

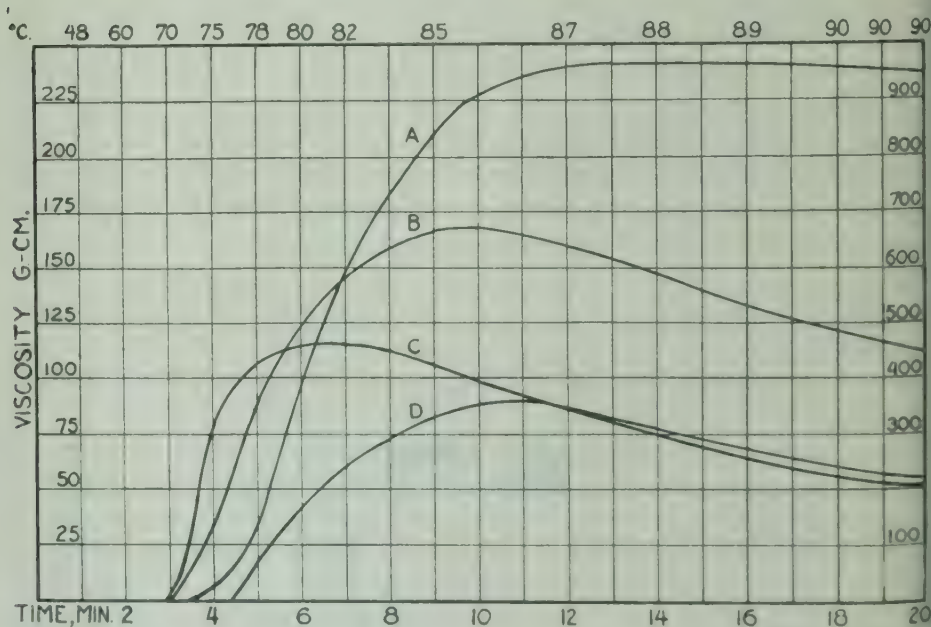


Fig. 19 : 7. Corn Industries viscometer curves of 8% corn starch pastes. (A) Unmodified. (B), (C) and (D) Acid modified. (B) Alkali fluidity 40. (C) Alkali fluidity 20. (D) Alkali fluidity 60. Viscosity scale for (A) and (C) at right ; for (B) and (D) at left.

properties including the effect of rate of heating, final paste temperature, concentration, pH and defatting of corn starch.¹¹⁹ Use of the viscometer for studying enzyme conversions and cooling curves has also been reported.¹²⁰

Cold Gelatinising Agents.—Not only does hot water gelatinise starch to form pastes, but many inorganic and organic chemicals cause starch to gelatinise in cold water. These have been studied extensively by many investigators and their effects are described elsewhere in this book. Several methods of evaluating starches based on the use of added chemicals have been proposed. Among these are the thiocyanate viscosity method of Richardson⁷⁷ and of Jambuserwala.⁷⁸ Methods based on the use of soap have been proposed by Houtz,⁷¹ Heald,⁷⁹ and Kesler and Black.⁸⁰ However, the only method of this type which has come into general use is the alkali fluidity procedure first described by Buel⁴⁶ which is used regularly in the corn starch industry for characterising certain kinds of starch products.

Alkali Fluidity Test. It has been found that for starches of one variety and of one method of modification the alkali fluidities increase regularly with the extent of modification and can be used to predict the properties of the pastes cooked in the usual manner. For example, acid-modified corn starches are often sold on the basis of their fluidity and this usually refers to their alkali fluidity number. It should be noted that where starches of different kinds are compared, the alkali fluidities do not give the same relative values as the pastes prepared by cooking the starches with water. If, for example, corn starch and tapioca starch of the same alkali fluidity number are cooked, it is found that their viscosities are quite different. Similarly if two starches are manufactured by different processes they may have the same alkali fluidity number but will give cooked pastes which differ widely. Nevertheless, when its limitations are understood, the method is of great value and is frequently used both for factory control of the modifying process and as a specification for the finished product.

Various procedures and funnels are in use⁴⁹ but the following directions are typical. The fluidity funnel is an ordinary glass funnel of 4-inch diameter with the stem cut short. A glass tube of the same diameter as the stem is drawn out to form an orifice about one-sixteenth inch in diameter. Funnel stem and tube are joined by a short piece of rubber tubing, so that the total length of stem and tip is about 3 inches. The tip is made so that when 110 ml. of distilled water at 75° F. is in the funnel, 100 ml. will flow out in 70 seconds. (As stated above, any such funnel should

be further standardised by use of other liquids of higher viscosity.)

Five grams of starch is placed in a 250 ml. beaker to which 10 ml. of distilled water is added, and a smooth slurry made. Then 90 ml. of 1 per cent. sodium hydroxide at 75° F. is added and the paste is stirred for 3 minutes at about 70 r.p.m. It is then placed in a water bath maintained at 75° F. where it remains for 30 minutes without stirring. The fluidity funnel is also immersed in the bath until 3 minutes before the test is made, when it is removed and is allowed to drain. A finger is held under the tip, the funnel is tilted somewhat, then the paste is poured in carefully so that the stem is filled and free from bubbles. A 100 ml. graduated cylinder is placed under the tip and the paste is allowed to flow. The volume of paste which flows in 70 seconds, timed with a stopwatch, is the alkali fluidity.

Gel Testing.—When the more concentrated pastes of certain starches stand at room temperature for a few hours they set to rigid gels. Because of this property they are used in the food industry for some candies, puddings, and other products,⁸¹ and for other industrial purposes. Evaluation of the gel properties of starches intended for such uses is essential to ensure suitability of the product.

Properties of starch gels can be determined with accuracy only if the same precautions are followed in cooking the starch that were given for viscosity determinations. In addition, the tests must be made under carefully standardised conditions. The strength of gels depends on the time of setting, the temperature at which they are stored and tested, the dimensions of the mould, and in some testing methods on the nature of the surface. In unpublished work of Bechtel, it has been found that starch gels increase in strength rapidly during the first 10 hours and that during the period from 18 to 24 hours there is little change. With increase in temperature the strength decreases rather rapidly above 12° C. and the decrease accelerates as the temperature rises. Furthermore, if tests are made with a plunger without removing gels from their moulds there will be effects due to the walls and bottom unless the mould has a diameter several times that of the plunger, and the gel has a depth of at least 1½ inches. If a starch gel is allowed to set with the surface exposed to air, even in a well-filled, stoppered jar, a tough skin may form which destroys the value of any test made through it. It is not advisable to remove the skin before testing, for this alters the properties of the gel. Formation of the skin is often prevented by covering the surface with kerosene immediately after pouring the hot paste into the mould. A method of avoiding this effect

is to remove the gel from the mould and test it through the bottom.⁸² In addition, results of tests depend on the rate at which the load is added to the gel, so precautions must be observed to keep this reasonably constant.

A number of methods have been proposed for testing gel properties. Descriptions of the older ones are given by Sheppard⁸³ and Alexander.⁸⁴ In general, the methods employed measure either the force required to break the gel, or the deformation of the gel caused by applying a definite load. Since different properties are measured in the two types of tests there is no general relationship between them.^{85, 88} This has led to the development of instruments which make both measurements.

The terms 'gel strength' or 'jelly strength' are often used loosely by various investigators for either of the properties given above. Studies by Brimhall and Hixon⁸⁵ show that the resistance of starch gels to deformation is true rigidity⁸⁶ and that results can be expressed in absolute units if measurements are made in an apparatus capable of such standardisation.

Rough determinations of relative rigidity may be made by pressing the surfaces of a series of gels with the finger tips or by removing them from the mould and observing the deformation from the shape of the mould.⁸⁷ Such determinations are not adequate for work of high accuracy, and because no numerical value can be given to the result they are not suitable for comparisons of gels prepared at different times.

Many gel testers have been described in the literature, especially for testing glue, gelatine, and pectin gels. Most of these have not been successfully applied to starch testing, because as a rule they are not sufficiently sensitive and precise for measuring the properties of starch gels, which are generally far less strong.

Rigidity. The rigidometer of Brimhall and Hixon⁸⁵ consists of a tall cylinder with a long narrow tube suspended in it from a torsion wire. The head of the wire is equipped with a pointer and the top of the jar has a graduated scale. A paste is poured into the cylinder, the tube is centred, and the paste is allowed to form a gel. The wire is twisted an arbitrary amount and the resulting turn of the tube is measured by the deflection of a beam of light reflected from a mirror on the tube to a large scale. Care must be exercised that the wire is not twisted through an angle great enough to shear the gel, as this would destroy the value of the measurements. Torsion wires may be calibrated in absolute units so that the modulus of rigidity can be calculated.

The Bloom gelometer⁸⁹ which is used in the glue and gelatine industry is sometimes used for starch gels of high concentration.

This instrument measures the weight required to produce a depression of 4 mm. depth in the gel by a cylindrical plunger 12.5 mm. in diameter. Weight is added to the plunger in the form of lead shot, the addition of which is controlled automatically by electrical contacts. The result of the test is known as the 'Bloom number,' which is a measure of relative rigidity.

Breaking Strength. The Tarr-Baker jelly tester,^{90, 91} is frequently used⁸⁷ for evaluating breaking strength. A plunger is slowly forced into a gel by an increasing head of water. By means of a manometer the pressure is read at which the plunger breaks the gel.

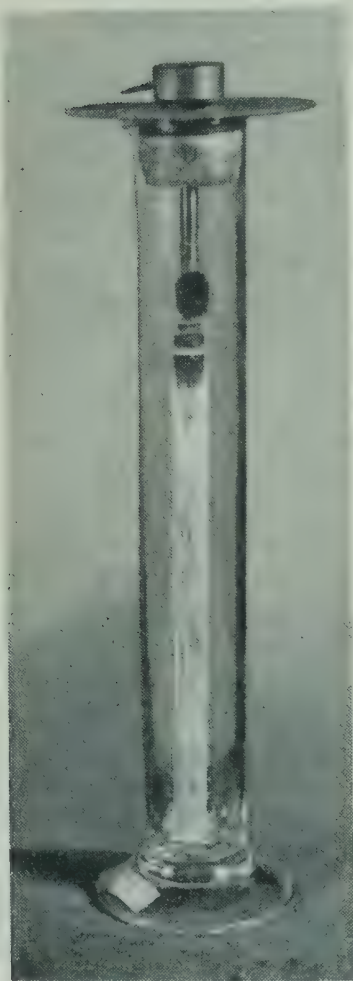


FIG. 19 : 8.—The rigidometer of Brimhall and Hixon.

The method of Saare and Martens⁹² is also used.⁹³ In this procedure a disc of standard size is suspended horizontally by a rod attached to the centre of one side at a definite depth in a paste which is then allowed to gel. The jar containing the gel is placed on a bridge above the pan of a balance and the rod is attached to the beam. Weight is added to the opposite pan at constant rate, usually by pouring lead shot, until the disc breaks the gel. Recently an improvement of this method was reported by Hamer¹²¹ who places the jar with the gel on an adjustable platform above the balance pan. He adds mercury at constant rate to the other pan and adjusts the platform so that the balance beam is maintained horizontal. In this way he obtains the breaking strength with greater precision than heretofore, and from the change in height of the platform he gets a measure of the deformability of the gel under load before it breaks. Hamer has reported the

effect of size of the disc, its depth, gel temperature, and the rate of adding load, and demonstrates the necessity of a standardised method for precise results. The embedded-disk principle has been used recently by Bechtel¹²⁹ in a gelometer suitable for rapid testing of both relative rigidity and breaking strength of starch

gels. This gelometer has been found to be very sensitive to slight differences in gel properties, and to give results of high precision.

The tube penetrometer of Fuchs⁹³ consists of a sharpened metal tube similar to a cork borer attached to a metal shaft which is held in a vertical position by two bearings. A weight is placed on a small platform on the top of the shaft, the penetrometer is released, and the time is noted for the instrument to cut a measured distance into the gel. The usual commercial penetrometers have not been found satisfactory, in general, for testing starch gels because they lack the requisite sensitivity.

Rigidity and Breaking Strength. Hixon and Brimhall⁸² have developed a gelometer for measuring both relative rigidity and breaking strength of starch gels. It is designed especially for gels of 6 to 9 per cent. concentration. The paste is allowed to gel in a 400 ml. beaker from which it is removed and placed bottom down on a level platform which has a circular hole at the centre. This procedure avoids the effect of skin and ensures testing a smooth level surface. Suction is applied at a slow constant rate through the hole in the platform. Readings of suction are made on a manometer, while corresponding deformation is measured by the height of a column of water. The test may be continued until the gel breaks, and thus in a single test both relative rigidity and breaking strength are found. They have shown that relative rigidities measured with the gelometer correspond well with measurements made with their rigidometer.

Another instrument suggested for this purpose is the gelometer of Saxl.⁹⁵ It consists of a sensitive balance, on the platform of which the gel is placed. By means of a counterpoise on a beam the balance is adjusted to zero. A plunger is then moved by a rack and pinion until it is just in contact with the gel. The plunger is lowered a measured distance and weights are added to the opposite side of the balance until it is again at zero. A series of readings may be obtained which give the relative rigidity and finally the 'yield point' at which, without further addition of load, the plunger penetrates the gel. Moreover, compressive loads can also be systematically decreased so that it is possible to use the instrument to measure quantitatively an entire hysteresis loop, and what Saxl terms the dynamic characteristics of plastic materials. By this means the elastic recovery of a gel can be determined, and the line of demarcation found between permanent plastic deformation and elastic recovery, before the material has been stressed beyond its yield point. It has been found in this laboratory that the Saxl gelometer is sufficiently precise and sensitive to show marked differences between commercial grades of acid-modified corn starch.

Syneresis. On being allowed to stand, starch gels, like others, tend to lose water leaving a more concentrated gel. This process of ageing is called syneresis. A study of the syneresis of starch gels was made by Chapman and Buchanan,⁹⁶ who found that the amount of syneresis increases with the surface exposed, and with age. With increase in starch concentration it decreases, while the length of cooking the paste has little effect. Acetates, sulphates, oxalates and citrates were found to increase syneresis, while many other salts retard it. Of the salts tested, those most effective in retarding it were chlorides of calcium, strontium and barium, sodium iodide, trisodium phosphate and potassium

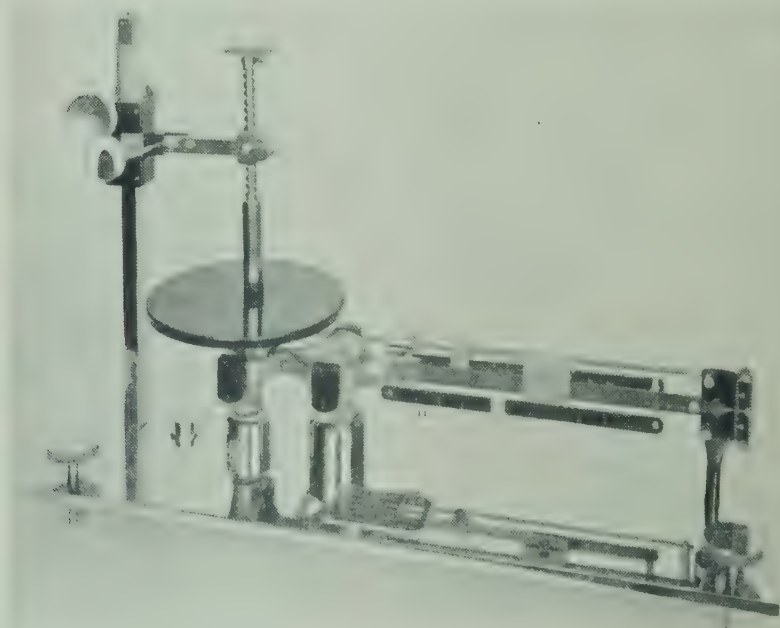


FIG. 19 : 9.—The Saxl gelometer.

(By courtesy of Erwin J. Saxl.)

sulphocyanate. No relationship was found between granule size and the extent of syneresis. It is an undesirable property, and the best starches for gels are those with this property at a minimum.

A method of evaluating syneresis is as follows. Gels are made under identical conditions of cooking and storage. When the gel is firm it is carefully removed from the mould so that the structure is not damaged, and is placed on a sheet of filter paper in a place free from drafts and at a uniform temperature. After definite intervals the distance the water has travelled in the filter paper is measured. The best starches produce the smallest water rings.

Gelatinisation Temperature.—When a starch is heated with water the granules lose their birefringence, then as the temper-

ature rises they swell to several times their original size, the viscosity begins to increase, and the appearance changes from that of a cloudy suspension to a translucent paste. These changes occur in temperature ranges which are characteristic of the type of starch and the nature and extent of its modification. This makes observations of the temperatures at which they occur of value in the differentiation and identification of starches.

Much research has been conducted in this field, in which all

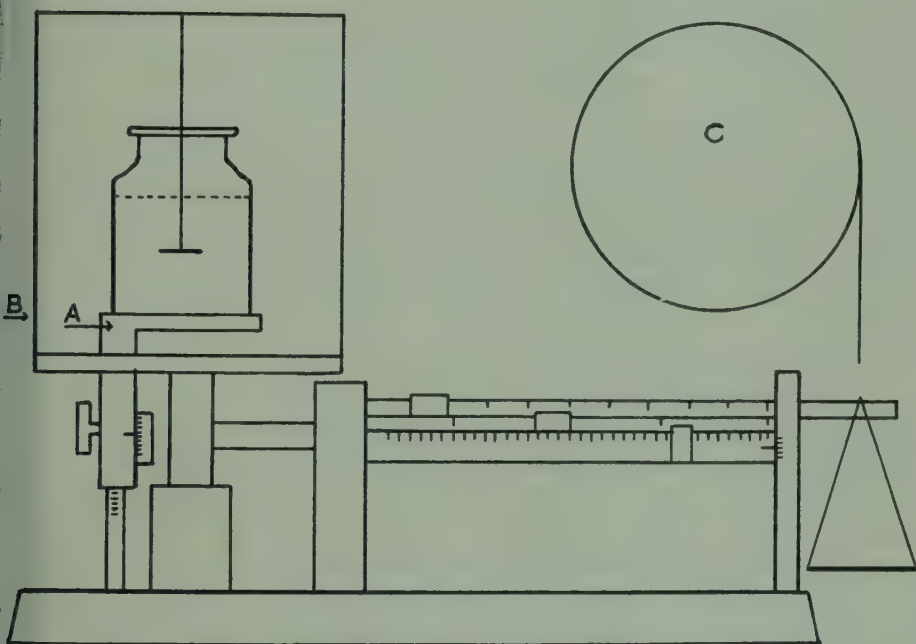


FIG. 19 : 10.—Schematic drawing of embedded-disk gelometer. A is a platform adjustable in height. B is a frame attached to the pan of a triple-beam laboratory balance. C represents a means of applying a continuously increasing load to the disk.

of the kinds of change given above have been used for the determination of gelatinisation range, the range of temperature in which the observed change occurs. Since the changes do not occur simultaneously,²⁵ it is apparent that the gelatinisation range found depends on the property observed. In the older literature a gelatinisation point was often given. This is misleading, because some granules of a given starch will undergo any of the above changes at a lower temperature than others. The gelatinisation point is thus specific for each granule, but of doubtful significance when applied to a sample of starch. For this reason it is now more usual to determine the gelatinisation range.

A factor which must not be overlooked is that gelatinisation range is influenced by the conditions of the test. Alsberg and Rask⁹⁷ showed that the *pH* of the sample, the rate at which it is heated, and the extent to which the starch has been dried previous to the test all affect the result. The presence of added chemicals may also have an effect, and at least in most methods the result depends on the concentration at which the starch is tested.

Loss of Birefringence. A small quantity of starch may be suspended in water in a test tube and slowly heated in a water bath. Samples are taken at regular temperature intervals and are examined under a polarising microscope. Or the suspension may be heated in a microscope hot stage using electricity⁹⁸ or hot water.⁹⁹ Various points have been taken as the gelatinisation temperature. Nyman¹⁰⁰ reported the temperature at which birefringence disappeared in the larger granules, Reichert¹⁰¹ reported the temperature of disappearance in most granules, while that of complete disappearance was taken by Francis and Smith.⁹⁹ Dox and Roark⁹⁸ chose the temperature of disappearance of birefringence in all granules large enough to show the characteristic shape and markings.

Translucency. Samec¹⁰² observed that if an incandescent light bulb is immersed in a glass vessel containing a starch suspension which is being heated, a sudden change in translucency occurs at a definite temperature. Cook and Axtmeyer¹⁰³ devised a procedure by which a beam of light is passed through a starch suspension and actuates a photoelectric cell connected to a microammeter. Readings of current and temperature are made and the results when graphed give curves showing the beginning of gelatinisation and the range. Cook and Axtmeyer stated that the method is capable of accurate duplicability and that it is suitable for the identification of starches and for determining the treatment given them during manufacture.

The method of Cook and Axtmeyer was refined by Morgan¹⁰⁴ who made a study of the gelatinisation range of a large number of commercial starches. Characteristic curves were obtained for each kind of starch, and modification of the starch could be followed by the changes in the curves, for with increased modification gelatinisation was found to occur at progressively lower temperatures. Morgan also showed the application of his method to the quantitative analysis of mixtures of starches. An interesting feature of the method is that only 0.33 gram of starch is needed. The suspension is heated at a constant rate of 2.5° C. per minute so that the test can be completed in half an hour. Kuntzel and Doehner¹⁰⁵ used a similar method but included a

recorder to obtain the transmission-temperature curve automatically.

Refractometric Method. A rapid optical method of great convenience which has been developed in the laboratory of Penick & Ford is based on the use of an Abbe refractometer. The starch suspension is heated slowly, and at regular intervals a drop is transferred to the refractometer and the refractive index is read. During gelatinisation the refractive index rises from zero to a maximum. It is graphed against temperature, giving a curve which is characteristic of the kind of starch and the degree of modification. The method has proved to be sensitive and capable of accurate duplication.

Viscosity. Ostwald¹⁰⁶ used the increase in viscosity of starch paste as a means of determining gelatinisation points, making a series of viscometric tests at increasing temperatures. He regarded as the gelatinisation point the temperature at which viscosity showed a sudden large increase. Alsberg and Rask⁹⁷ studied the gelatinisation of wheat and corn starches by determining viscosity at various temperatures using the Stormer viscometer. Their results show that the increase in viscosity with rising temperature is a gradual process taking place over a range of 25 to 30 degrees. They therefore concluded that there was no definite temperature of gelatinisation, but rather a gelatinisation range. The newer viscometers by which a viscosity-temperature curve is recorded, or by means of which a series of readings can be made readily, are well suited for the determination of gelatinisation range. A great advantage of these instruments for this purpose is that the gelatinisation range is found in the same test that gives the viscosity curve. This method appears to be equally as sensitive as any other.

Moisture.—A comprehensive study of the problems involved in the accurate determination of moisture in starch has been made by Sair and Fetzer.¹⁰⁷ They found that moisture can be removed completely without causing decomposition of the starch, either by distillation with toluene using a modification of the Bidwell-Sterling method,¹⁰⁸ or by heating it in a vacuum oven to constant weight at 100° C. At an oven temperature of 135° C. it was found that dextrans and highly modified starches lost volatile matter other than water. Another finding of great importance was that starch heated for as long as 40 hours at 100° C. in an air oven gave a moisture analysis about 1 per cent. below that obtained in the vacuum oven. Their methods with the precautions given in their original article, are suitable for reference methods of great accuracy.

It is often desirable in practice to use rapid oven methods. One frequently used routine procedure is to heat 5 grams of starch in a metal moisture dish for 4 hours in a vacuum oven at 105° C. The official German method requires that 5 grams of starch be heated for 1 hour at 50° C. then 3 hours at 120° C. in an air oven.¹⁰⁹ There are available various rapid moisture testers by means of which a moisture value can be obtained in a few minutes. Such arbitrary methods should be used only after comparison of the results with one of the reference methods. A correction chart may then be made for obtaining true moisture-content from the results of the rapid test.

Foreign Matter.—When starch is to be used for food or for paper coating the presence of foreign matter is very undesirable, and the determination of the amount and its nature is essential.

Several methods are available for the separation of foreign matter from starch. One rapid method which is frequently used is to sieve a definite weight of dry powdered starch through a 200-mesh screen or through No. 17 bolting silk until the starch has passed the screen leaving upon it the foreign matter. Another is to suspend 50 grams of starch by stirring in 500 ml. of distilled water. The suspension is then passed through a layer of No. 16 or No. 17 bolting silk. Other methods are presented in a handbook prepared by the U.S. Food and Drug Administration,¹¹⁰ including procedures applicable to food products which contain starch.

If the starch is oily, as in the case of confectioners' moulding starch, it is advisable to remove the oil by washing it with acetone. This greatly improves its sieving properties. Acetone is to be preferred to ether or petroleum ether because if the starch is to be suspended in water prior to sieving, the acetone will dissolve readily.

When the foreign matter has been separated from the starch its amount may be estimated. The nature of the particles may be determined by microscopic examination. The handbook referred to above¹¹⁰ has proved of great value for the identification of foreign matter as it gives a discussion of methods of microanalysis which may be employed, and descriptions and illustrations of various kinds of contamination which may be present.

Odour.—Examination for odour is made to determine possible rancidity of the fat present in cereal starches, and mouldiness which may be due to poor storage conditions. One method is to place a quantity of starch in a flask or beaker, then add water at 160 to 170° F., stir quickly and note the odour. Another and less rapid method is to place the starch in a jar with a tight-fitting top

and heat it for 16 hours at 130° F. As soon as the jar is opened the odour is noted. Unpleasant odours can be detected readily by either procedure.

Hydrogen Ion Activity.—The problems encountered in measuring the pH of suspensions of starch in water were investigated by Ripperton.¹¹¹ His work shows that the observed pH changes with starch concentration up to 5 per cent., above which it is constant. He found that if the starch is allowed to settle and the test made on the supernatant liquid, the observed pH is somewhat different from that of the suspension, and that it is not constant. To reach equilibrium it was found that the suspension must be stirred for 10 to 15 minutes. The usual procedure for determining pH is to suspend 1 gram of starch in 9 ml. of distilled water with thorough stirring. The pH is then determined electrometrically before the starch settles out.

It has been found in some cases when a glass electrode is used that starch coats the electrode, with the result that the determinations are erratic. This can be prevented by stirring the suspension during the test and by making it as rapidly as possible.

Colour.—Several methods are in use for the determination of colour in starch products, ranging from visual inspection to the use of a photometer. One very simple method is to place a small pile of starch on a porcelain plate and place adjacent to it similar piles of starches which have been selected as colour standards for matching. By means of a clear glass plate the piles are carefully flattened so that they touch each other to form a continuous layer. The sample is compared with the standards by observing them in diffused daylight. It matches the standard when no boundary can be seen.

Another method consists in extracting the coloured material by suspending 10 grams of starch in 200 ml. of 2 per cent. alcoholic sodium hydroxide. The suspension is heated to boiling, then is cooled for 30 minutes with continuous shaking. After filtering, the liquid is compared with standards by use of a colorimeter. This method is based on the assumption that the colour is due to alcohol soluble materials, which is not always true.

The Lovibond tintometer is often used. The colour reflected from a smooth surface of powdered starch is matched by interposing standard Lovibond series 200 red and series 510 yellow colour glasses in the light reflected from the smooth white surface of a magnesia block placed beside the sample.

Various visual or photoelectric spectrophotometers of the reflectance type are also used. The chief precaution in any

measurement is to use powdered starch to ensure the observation of a smooth surface.

Flow Properties or Mobility of Dry Starch.—The readiness with which powdered starch flows can be measured by shaking a definite amount of the dry starch in a covered sieve, using a mechanical shaking device to ensure uniformity for all samples. The amount of starch which passes through the screen in a definite time is a measure of its mobility.⁹⁴ Another and very easily performed test is to place a small sample of powdered starch of standardised size and conical shape on a horizontal glass plate which can be inclined and behind which is a scale showing the angle of inclination. The plate is slowly inclined at a constant rate and the angle is noted at which the starch begins to slide. The more mobile starches flow at a smaller inclination.

Water Soluble Material.—Determination of the amount of water soluble matter in starch is of value because it gives an indication of the presence of added materials. In a dextrinised product it is also useful as a means of determining roughly the degree of conversion, for the more highly converted dextrans and gums contain larger amounts of soluble constituents.

Methods for determining the amount of water soluble material all depend on suspending starch in water at a definite temperature and concentration. The suspension is maintained by agitation, then is filtered and the filtrate analysed.

One typical procedure is to suspend 10 grams of starch in distilled water to a total volume of 200 ml. The flask is shaken vigorously each half-hour for 3 hours. This must be done at constant temperature duplicated for all tests. The suspension is filtered and an aliquot of 20 ml. of the filtrate is evaporated to dryness on a steam bath. It is then dried to constant weight in an oven at 105°C. and the residue is weighed.

Other Properties.—Certain other characteristics of pastes of different starches are used in comparing or differentiating them, and although the tests are qualitative in nature, the observations are frequently of great value. One of these is the relative opacity of pastes. When pastes at the same concentration are compared it is found that those of ordinary cereal starches are more opaque than those of root or waxy cereal starches.

Differences in texture may likewise be observed. If paste is allowed to flow from a stirring rod some pastes break abruptly. These are termed 'short' pastes. Others are more cohesive and form a long string. They are called 'long' pastes. Unmodified tapioca and potato starches form 'long' pastes while those of unmodified corn and wheat are 'short'. Galloway¹¹² has

discussed long and short pastes and believes that differences are due to the effective volumes and deformability of the swollen granules.

Dextrins and Gums.—In general, the methods already given for starches are also applied to the examination of dextrins and gums. An excellent example of the use of several of these techniques is given by Brimhall,¹¹³ who used oxidation with periodate, amylose content, solubility, the action of enzymes, end-group analysis, copper-reducing number and alkali lability in her study of pyrodextrins.

Viscosity. Because the viscosity of these products usually is so much lower than that of starches, tests are made using much more concentrated pastes. From 30 to 50 per cent. or even higher concentrations may be used, depending on the product tested. An orifice or pipette viscometer is used industrially and it may be jacketed with a water bath to maintain constant temperature. The dextrin is made into a smooth suspension with cold water and is then cooked to 85° C., after which it is cooled to some standard temperature and the viscosity test is made. The temperature chosen is usually near room temperature. If the dextrin is to be used in an adhesive which contains borax, the same proportion of borax is added to it before cooking it for the viscosity test. This is necessary because the effect of borax in altering viscosity differs with the type of product. It should be noted that the addition of 0.5 to 1 per cent. of sodium hydroxide, based on the weight of dextrin, increases the effect of the borax and this must be considered in testing.

Some dextrins and gums, when prepared as pastes, thicken or 'set back' and turn cloudy on standing. For some purposes this is a disadvantage. The extent of set-back may be determined by making a viscosity test after 24 hours and comparing the result with that found immediately after cooling the paste.

Alkali Fluidity Test. The alkali fluidity test described above has been modified in the Penick & Ford laboratory so that it can be applied to the evaluation of dextrins and gums. For this purpose either 20 or 40 grams of the dextrin is used, depending on the degree of modification. This is suspended in 50 ml. of distilled water at 75° F., then 50 ml. of 4 per cent. sodium hydroxide at the same temperature is added. The other details of procedure are the same as those previously given. The method is subject to the same limitations as when applied to starches. That is, it cannot be used to predict the paste properties of dextrins from different varieties of starch, nor those products prepared by different processes. It is a valuable means of factory control of

the extent of dextrinisation, of specification of finished product, and of comparing different dextrans and gums.

Water Soluble Material. The amount of water soluble material present is used to obtain information about the extent of conversion of the dextrin and its suitability for certain purposes. A method for this determination is to suspend 20 grams of dextrin in 200 ml. of distilled water, at a definite temperature such as 20° C. The suspension is shaken mechanically for 30 minutes at this temperature and is filtered. Since in a pure dextrin the soluble matter consists entirely of starch conversion products, the concentration can be determined in the filtrate by a refractometer, as shown by Tolman and Smith.¹¹⁴ If the refractometer has a sugar scale the concentration is given directly, otherwise it may be obtained from refractive index-percentage sucrose tables which may be found in any handbook on sugar, such as that of Browne and Zerban.¹¹⁵ Dipping refractometers are very convenient and rapid, and pocket refractometers have proved of great value in the factory. Concentrations may also be measured directly by means of a Brix hydrometer. The concentration read must be multiplied by 10 to obtain the percentage of soluble carbohydrate since the dextrin was made in a 1 to 10 solution for the test.

Other Tests. It is frequently necessary to ensure uniformity in the colour of dextrans to be used for certain purposes such as in paper coating. Flavour and odour are important when dextrans are used in foods. In addition, pH, acidity or alkalinity and moisture-content must often be controlled. Sometimes tests for reducing sugars must be made as a means of determining the extent of conversion. For this purpose any standard procedure may be used.

REFERENCES

1. J. R. KATZ, *Textile Research*, 1938, **9**, 69.
2. T. J. SCHOCH and C. C. JENSEN, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 531.
3. T. C. TAYLOR, H. H. FLETCHER, and M. H. ADAMS, *Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 321.
4. T. C. TAYLOR and G. M. SALZMAN, *J. Am. Chem. Soc.*, 1933, **55**, 264.
5. F. F. FARLEY and R. M. HIXON, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 616.
6. W. A. RICHARDSON, R. S. HIGGINBOTHAM and F. D. FARROW, *J. Textile Inst.*, 1936, **27**, T131.
7. F. L. BATES, D. FRENCH, and R. E. RUNDLE, *J. Am. Chem. Soc.*, 1943, **65**, 142.
8. E. J. WILSON, JR., T. J. SCHOCH, and C. S. HUDSON, *J. Am. Chem. Soc.*, 1943, **65**, 1380.
9. T. J. SCHOCH, *J. Am. Chem. Soc.*, 1942, **64**, 2957.
10. R. L. WHISTLER and G. E. HILBERT, *J. Am. Chem. Soc.*, 1945, **67**, 1161.
11. J. M. NEWTON, F. F. FARLEY, and N. M. NAYLOR, *Cereal Chem.*, 1940, **17**, 342.

12. B. BRIMHALL and R. M. HIXON, *Cereal Chem.*, 1942, **19**, 425.
13. G. BARR, *A Monograph of Viscometry*, London, 1931, Chapter 11.
14. G. BARR, loc. cit., pp. 279-280.
15. G. BARR, loc. cit.
16. G. BARR, loc. cit., Chapter 4.
17. G. BARR, loc. cit., Chapter 8.
18. F. D. FARROW and G. M. LOWE, *J. Textile Inst.*, 1923, **14**, T414.
19. F. D. FARROW, G. M. LOWE, and S. M. NEALE, *J. Textile Inst.*, 1928, **19**, T18.
20. C. L. ALSBERG, *Ind. Eng. Chem.*, 1926, **18**, 190.
21. W. GALLAY and A. C. BELL, *Can. J. Research*, 1936, **B14**, 360, 381.
22. W. GALLAY, *Can. J. Research*, 1936, **B14**, 391, 409.
23. J. R. KATZ, M. C. DESAI, and J. SEIBERLICH, *Trans. Faraday Soc.*, 1938, **34**, 1258.
24. T. C. TAYLOR and C. O. BECKMANN, *J. Am. Chem. Soc.*, 1929, **51**, 294.
25. T. J. SCHOCH, *Cereal Chem.*, 1941, **18**, 121.
26. C. M. McDOWELL and F. T. USHER, *Proc. Royal Soc.*, London, 1931, **131A**, 409, 564.
27. M. BLINC and M. SAMEC, *Cong. intern. tech. chim. ind. agr., Compt. rend. 5th Congr.*, 1937, *Sec. 15*, 214.
28. E. HATSCHKE, *The Viscosity of Liquids*, London, 1928.
29. E. C. BINGHAM, *Fluidity and Plasticity*, New York, 1922.
30. E. C. BINGHAM, loc. cit., p. 324.
31. W. HARRISON, *J. Soc. Dyers and Colorists*, 1911, **27**, 84.
32. W. A. RICHARDSON and R. WAITE, *J. Textile Inst.*, 1933, **24**, T383.
33. M. SAMEC, *Kolloid Chemie der Starke*, Dresden, 1927, pp. 265-282.
34. H. G. B. DEJONG, *Rec. Trav. Chim.*, 1924, **43**, 189.
35. J. C. RIPPERTON, *Ind. Eng. Chem. Anal. Ed.*, 1931, **3**, 151.
36. C. A. ANKER and W. F. GEDDES, *Cereal Chem.*, 1944, **21**, 346.
37. E. WIEGEL, *Zeit. Spiritusind.*, 1933, **56**, 62.
38. C. WIEDMER, *Tiba*, 1936, **14**, 103, 107.
39. G. M. MACNIDER, *J. Ind. Eng. Chem.*, 1912, **4**, 417.
40. G. G. PIERSON, *Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 183.
41. T. CHRZASZCZ and J. JANICKI, *Biochem. Zeit.*, 1932, **256**, 252.
42. W. A. NIVLING, *Starches, Their Fluidity and Viscosity in Relation to Sizing Value for Textiles*, New York, 1912, pp. 2-12.
43. *U.S. Federal Standard Stock Catalog JFF-S-701, Sec. IV, Part 5*, Dec. 5th, 1933, p. 3.
44. W. F. A. ERMEN, *J. Soc. Chem. Ind.*, 1907, **26**, 501.
45. G. M. MACNIDER, *Ind. Eng. Chem.*, 1917, **9**, 597.
46. H. BUEL, *8th Intern. Congr. Appld. Chem.*, Washington and New York, *Orig. Comm.*, 1912, **13**, 63.
47. L. BALDERSTON, *J. American Leather Chemists Assn.*, 1913, **8**, 47.
48. M. L. SHEELY, *Ind. Eng. Chem.*, 1923, **15**, 1109.
49. W. L. MORGAN and N. L. VAUGHN, *Ind. Eng. Chem.*, 1943, **35**, 232.
50. C. A. BRIGGS and J. L. MCCARTHY, *Paper Trade J.*, 1942, **114**, No. 4, 37, Jan. 22nd.
51. T. CHRZASZCZ and S. PIOROZEK, *Zeit. Spiritusind.*, 1910, **33**, 66.
52. O. S. RASK and C. L. ALSBERG, *Cereal Chem.*, 1924, **1**, 7.
53. S. N. GLARUM, *American Dyestuff Reporter*, 1934, **23**, 175.
54. M. M. MACMASTERS and G. E. HILBERT, *Ind. Eng. Chem.*, 1944, **36**, 958.
55. J. A. GEDDES and D. H. DAWSON, *Ind. Eng. Chem.*, 1942, **34**, 163.
56. G. F. C. SEARLE, *Proc. Cambridge Phil. Soc.*, 1912, **16**, 600.
57. R. F. MACMICHAEL, *Ind. Eng. Chem.*, 1915, **7**, 961.
58. W. H. HERSCHEL, *Ind. Eng. Chem.*, 1920, **12**, 282.
59. W. H. HERSCHEL, *J. Optical Soc. America*, 1923, **7**, 335.
60. E. G. BAYFIELD, *Cereal Chem.*, 1934, **11**, 121.
61. P. E. MEISS, R. H. TREADWAY, and L. T. SMITH, *Ind. Eng. Chem.*, 1944, **36**, 159.
62. W. H. GIBSON and L. M. JACOBS, *J. Chem. Soc.*, 1920, **117**, 473.

63. E. VALENTA, *Chem. Ztg.*, 1906, **30**, 583.
64. F. HÖPPLER, *Zeit. Techn. Physik.*, 1933, **4**, 165.
65. R. WOBSE and FR. MÜLLER, *Kolloid-Beihefte*, 1941, **52**, 165.
66. I. E. KOMM and U. MARTIN, *Vorratspflege u. Lebensmittelforsch.*, 1939, **2**, 635, 650.
67. G. V. CAESAR, *Ind. Eng. Chem.*, 1932, **24**, 1432.
68. G. V. CAESAR and E. MOORE, *Ind. Eng. Chem.*, 1935, **27**, 1447.
69. J. A. RADLEY, *Starch and Its Derivatives*, New York, 1940, p. 43.
70. E. F. GLABE, *Cereal Chem.*, 1939, **16**, 661.
71. H. HOUTZ, *Paper Trade J.*, 1941, **113**, No. 6, 32, Aug. 7th.
72. H. N. BARHAM, J. A. WAGONER, and G. N. REED, *Ind. Eng. Chem.*, 1942, **34**, 1490.
73. H. N. BARHAM, J. A. WAGONER, B. M. WILLIAMS, and G. N. REED, *J. Agricultural Research*, 1944, **68**, 331.
74. H. N. BARHAM, J. A. WAGONER, E. H. HARCLERODE, and C. L. CAMPBELL, *Kansas Agricultural Experiment Station Bull.*, **61**, 1946.
75. C. W. BRABENDER, *Muhlelab.*, 1937, **7**, 121.
76. G. J. MÜLLER, *Cong. intern. tech. chim. ind. agri.*, *Compt. rend.*, 6th Congr., Budapest, 1939, **2**, 529.
77. W. A. RICHARDSON, *Chemistry and Industry*, 1939, **17**, 464.
78. C. B. JAMSEERWALA, *J. Textile Inst.*, 1941, **32**, T201.
79. A. M. HEALD, *Paper Trade J.*, 1941, **113**, No. 2, 39, July 10th.
80. C. C. KESLER and W. C. BLACK, *Paper Trade J.*, 1942, **114**, No. 21, 57, May 21st.
81. S. WOODRUFF and L. NICOLI, *Cereal Chem.*, 1931, **8**, 243.
82. R. M. HIXON and B. BRIMHALL, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 193.
83. S. E. SHEPPARD, *Gelatin in Photography*, Vol. 1, New York, 1923.
84. J. ALEXANDER, *Glue and Gelatin*, New York, 1923.
85. B. BRIMHALL and R. M. HIXON, *Ind. Eng. Chem. Anal. Ed.*, 1939, **11**, 358.
86. E. C. BINGHAM, *J. Rheol.*, 1930, **1**, 511.
87. S. WOODRUFF and M. M. MACMASTERS, *Illinois Agricultural Experiment Station Bull.*, **445**, 1938.
88. I. J. SAXL, *Physics*, 1936, **7**, 62.
89. F. L. DE BEUKELAER, *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 348.
90. L. W. TARR, *Delaware Agricultural Experiment Station Bull.*, **142**, 1926.
91. G. BAKER, *Ind. Eng. Chem.*, 1926, **18**, 89.
92. O. SAARE and P. MARTENS, *Zeit. Spiritusind.*, 1903, **26**, 436.
93. R. W. KERR, *Chemistry and Industry of Starch*, New York, 1944, pp. 97-98.
94. R. W. KERR, *loc. cit.*, p. 109.
95. E. J. SAXL, *Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 82.
96. O. W. CHAPMAN and J. H. BUCHANAN, *Iowa State College J. Science*, 1930, **4**, 441.
97. C. L. ALSBERG and O. S. RASK, *Cereal Chem.*, 1924, **1**, 107.
98. A. W. DOX and G. W. ROARK, *J. Am. Chem. Soc.*, 1917, **39**, 742.
99. C. K. FRANCIS and O. C. SMITH, *J. Ind. Eng. Chem.*, 1916, **8**, 509.
100. M. NYMAN, *Zeit. Nahr. Genussm.*, 1912, **24**, 673.
101. E. T. REICHERT, *Carnegie Inst. of Washington*, Publ. **173**, pt. 1, 1913.
102. M. SAMEC, *Kolloid-Beihefte*, 1912, **3**, 126; *Kolloidchemie der Starke*, Dresden, 1927, pp. 169-170.
103. D. H. COOK and A. J. AXTMAYER, *Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 226.
104. W. L. MORGAN, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 313.
105. A. KUNTZEL and K. DOEHNER, *Kolloid Zeit.*, 1939, **86**, 124.
106. W. OSTWALD, *Trans. Faraday Soc.*, 1913, **9**, 34.
107. L. SAIR and W. R. FETZER, *Ind. Eng. Chem. Anal. Ed.*, 1942, **14**, 843.
108. J. E. CLELAND and W. R. FETZER, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 858; 1942, **14**, 27, 124.
109. SPROCKHOFF, *Zeit. Spiritusind.*, 1929, **52**, 27.
110. MICROANALYSIS OF FOOD AND DRUG PRODUCTS, *Food and Drug Circular*, No. 1, Federal Security Agency, Washington, 1944.
111. J. C. RIPPERTON, *Hawaii Agricultural Experiment Station Bull.*, **63**, 1931.

12. W. GALLAY, *Can. J. Research*, 1936, **B14**, 409.
13. B. BRIMHALL, *Ind. Eng. Chem.*, 1944, **36**, 72.
14. L. M. TOLMAN and W. B. SMITH, *J. Am. Chem. Soc.*, 1906, **28**, 1476.
15. C. A. BROWNE and F. W. ZERBAN, *Sugar Analysis*, New York, 1941, pp. 1206-13.
16. J. W. MULLEN and E. PACSU, *Ind. Eng. Chem.*, 1942, **34**, 807.
17. R. S. HIGGINBOTHAM, *J. Textile Inst.*, 1947, **38**, T131; *Shirley Inst Memoirs*, 1946, **20**, No. 26, 1.
18. C. C. KESLER and W. G. BECHTEL, *Analytical Chem.*, 1947, **19**, 16.
19. W. G. BECHTEL, *Cereal Chem.*, 1947, **24**, 200.
20. W. G. BECHTEL and C. C. KESLER, *Paper Trade J.*, 1947, **125**, No. 16, 35, Oct. 16th.
21. W. J. HAMER, *J. Research Natl. Bur. Standards*, 1947, **39**, No. 1, 29.
22. H. J. SELLING and F. L. J. VAN LAMOEN, *Chem. Weekblad*, 1947, **43**, 602.
23. C. H. LINDSLEY and E. K. FISCHER, *J. Applied Phys.*, 1947, **18**, 988.
24. E. K. FISCHER and C. H. LINDSLEY, *J. Colloid Sci.*, 1948, **3**, 111.
25. W. G. BECHTEL, C. C. KESLER, and J. STINCHFIELD, *Starch for Paper Coating*, TAPPI Monograph Series, No. 3, New York, 1947, Chapter 11.
26. F. H. FROST, *ibid.*, Chapter 21.
27. W. G. BECHTEL and C. C. KESLER, U.S. Patent No. 2, 491, 639.
28. W. G. BECHTEL and E. K. FISCHER, *J. Colloid Sci.*, 1949, **4**, 265.
29. W. G. BECHTEL, *J. Colloid Sci.*, 1950, **5**, 260.

APPENDIX

NOTES ON THE SIGNIFICANCE OF PATENT REFERENCES

Contributed by C. PAINE, B.Sc. Hons. (Lond.).

AN adequate bibliography on a field of technology such as that relating to starch will inevitably contain many patent references, that is, references to patent specifications. Such references are a common source of misapprehension and misunderstanding in the mind of the general reader. The present notes are an attempt to set down briefly some of the main points which arise in considering patent references.

In most of the industrially important countries it is an accepted principle that a patent monopoly, that is a piece of legal property, may be granted to an inventor in return for a public technical description of his invention. A patent specification is the usual document through which an inventor may present the technical description of his invention and also attempt to define the scope of the invention which he seeks to monopolise as a piece of legal property. This dual function of a patent specification is a frequent source of misunderstanding by the general reader. Thus, whilst a patent specification once published will always remain as a piece of technical information, it may have ceased at any given time and place to signify a live piece of legal property. That is, the specification remains but the patent (granted monopoly) for the invention may be dead or may never have been granted at all. Some countries (e.g. Canada) do not publish printed specifications, but most of the important countries do so and copies are purchasable at a trivial cost (e.g. in Britain, 2s. from the Patent Office). It is obvious that such a copy is, like a textbook, physically transportable as technical information throughout the world. The patent monopoly which it may represent is, however, limited to a geographical area prescribed by the laws of the country from which the specification originates. Thus, for example, a British patent has legal force in the British Isles, Northern Ireland and the Isle of Man, but not in Eire or the British colonies or Dominions. India and Canada, for example, have their own separate patent systems. French and Dutch patents on the other hand extend their scope to all the colonies of their respective countries. It will be understood that a United States patent has no force in Britain, Germany, etc., and vice versa. The existence of a United States or other foreign specification may indicate, however, that there is a separate and corresponding British patent.

The maximum potential life of a patent as a piece of legal property

varies from country to country. In Britain it is sixteen years, France fifteen years, Germany eighteen years, U.S.A. seventeen years, and so forth. The date from which this potential life is calculated and the manner in which this date can vary is dealt with below, but first it must be made clear that the potential and actual lives of a patent are not necessarily co-terminous. Thus, in most important countries a patent once granted can only be kept in force as a piece of legal property by payment of renewal fees, usually at annual intervals from a prescribed date. If the renewal fees are not paid the patent dies, that is, its actual life as a legal instrument does not extend to the maximum potential life permissible under the laws of the country in question. A notable exception is the United States where a granted patent runs its full term of seventeen years without any payment of renewal fees being necessary.

As indicated above the maximum potential life (term of years) of a patent varies from country to country and, in addition, the starting point of this term of years also varies somewhat. In most countries this starting point is the date at which application for a patent was made in the country in question, after making due allowance for any priority the applicant may have claimed under International Convention (see below). A notable exception again is the United States, where the term of maximum potential life runs from the date of grant of the patent and not from the application date. Since the U.S. Patent Office handling is often lengthy and the interval between application and grant is correspondingly great it frequently happens that a patent monopoly may be in existence in the United States long after all corresponding patents on the same invention are dead.

Reference has been made above to International Convention. This is an international arrangement whereby countries which are parties to it permit a foreign applicant the optional privilege of retaining the application date of his home country as a basis for establishing priority for his invention provided certain conditions are fulfilled. One of the most important conditions is that he shall file his application claiming such privilege within twelve months of his home application date. In Great Britain there is a further important condition. A foreign inventor (say U.S.A.) wishing to claim 'convention priority', i.e. his home (U.S.A.) application date, under International Convention in Britain must file a *complete* specification (complete with claims) corresponding to his foreign application within twelve months and then within a prescribed time (eighteen months from his U.S. application date) such specification becomes available for inspection by the public at the Patent Office and typescript or photostat copies (*Note: not printed*) are purchasable. Such published specifications are correctly referred to as British applications (*not patents*) with a five-figure number followed by the year of application, e.g. Brit. applic. 14235/1940 or 14235/40. At this stage they still have to undergo British Patent Office examination and are not yet accepted (printed) specifications, may never become so or may ultimately be accepted in greatly modified form,

especially in respect of claims. Such circumstances (application under convention) are the only ones in which a British specification becomes available to the public for inspection earlier in its life than the issue of a finally accepted (printed) specification.

In many countries the issue of a printed specification is followed by an interval of a few months before formal grant of a patent monopoly. During this interval interested parties, given suitable grounds, may oppose the grant of a patent. If such opposition is successful the grant may be refused entirely or, more commonly, the scope of the ultimate grant may be restricted by amendment of the specification.

What has been said so far may appear complicated and it is perhaps permissible to attempt to summarise the main points in a crude symbolism at some risk of over-simplification. An invention may be regarded as the child of the inventor's brain. The father may seek to register birth (file patent applications) in one or more countries in the hope that his progeny's credentials as a potential citizen may be then accepted (applications accepted by Patent Offices) and that the child may come of age, that is, come to full legal status (grant of patent) and thus have value as a wage earner (profit from exploitation of a protected process or as a source of royalties). As we have seen, according to country, such children may never come of age. Their credentials may be found wanting (application rejected by a Patent Office) or they may be found to be ailing and suffer mutilation or death during the process of attempting a cure (opposition by outside parties). Even after coming of age they may not live to die peacefully of old age [maximum potential term]; they may die of under-nourishment (non-payment of renewal fees) or be mutilated or die of some disease diagnosed late in life [successful revocation proceedings by outside parties]. In short, judging by the outward signs of birth registration (patent references) it may appear that there is a large and prosperous family in existence but this may be misleading; the death rate may have been small or large. The determination of the exact situation and the health of all concerned is usually a matter for specialised inquiry and this is one of the functions of a patent agent through whom such inquiries can be made.

How can patent references in a bibliography on starch affect a manufacturer in the field of starch technology? Let us assume that the manufacturer is British. If a given reference is to a British patent still in force or to a foreign specification corresponding to which there is a British patent still in force, it serves as a warning that he may not operate such an invention without permission (formal licence, with or without payment of royalties) from the owner of the British patent rights. If the British patent is dead or if there is no British patent corresponding to the foreign specification in question, he is perfectly free, subject to there being no other over-riding British patent rights in existence, to put the invention to technical use himself without fee or licence. If a British patent reference is more than sixteen years old the patent may be regarded as dead (maximum term)

although the technical information in the specification, now free to all, may still be valuable and very much alive. A list of British patents still in force is published annually by the Patent Office but as in certain instances the correct interpretation of the list required some experience, it is probably better to have the assistance of a patent agent in determining whether or not a particular patent is in force, especially in important or dubious cases.

A further point is important. Absence of a live British patent for a particular process indicates freedom for anyone to manufacture by such a process but the export of goods so manufactured to a foreign country where a relevant corresponding patent still remains in force would constitute an infringement of that foreign patent unless a licence had been obtained from the owner of the patent beforehand.

It can sometimes happen that a British manufacturer after using a particular process, perhaps secretly, for many years is suddenly alarmed by the appearance of a British patent granted to a competitor for the same process. The situation thus arising, however, may not be serious for either party. The patent may remain a perfectly sound and legally valuable one notwithstanding such prior use. Likewise the prior user cannot now be prevented from continuing his own use of the process free of licence or payment of royalties. He must, however, make absolutely sure of his ground, namely, that his own use of the process was in fact prior to the date of the invention now patented by his competitor. Given the date of actual first manufacture, a patent agent can speedily advise on such a point.

From what has been written above we see that the main implications of a given patent reference may be analysed by keeping in mind the following points :

- (1) A patent specification has a dual function:
 - (a) to describe the technical nature of an invention ;
 - (b) to define that for which the grant of a legal monopoly is sought.
- (2) A monopoly granted under a given patent has:
 - (a) a limited geographical scope ;
 - (b) a fixed maximum term of years starting from a fixed date, usually the date of application for the patent or a date otherwise clearly stated on the specification (e.g. 'convention priority' date or, in U.S.A., date of grant).
- (3) A monopoly granted under a patent may, from a variety of causes, die long before the fixed maximum term.
- (4) In the absence of a live monopoly the technical information in a patent specification is free for all to use within the prescribed geographical area, also in such other parts of the world in which no live corresponding patent monopoly exists.
- (5) The existence of a live monopoly precludes others from the use of the relevant invention without a formal licence from the owner of the patent rights.

- (6) Where a foreign patent reference exists there may also be a live corresponding British patent in existence. Until this has been determined by expert search the exact patent position in Britain cannot be seen.

It should be emphasised that what has been written relates to normal, peace-time conditions. Circumstances were considerably altered by the outbreak of the last World War and there was new legislation to meet these circumstances. The possibility of obtaining compulsory licences under enemy-owned patents and other relevant matters are too complicated to be dealt with here and the advice of a competent patent agent should be sought where necessary.



PHOTOMICROGRAPHS¹

The following photomicrographs were in most instances reduced from a magnification of $\times 500$ diameters to $\times 320$ diameters. Where two photomicrographs of identical fields appear on the same page, it will be observed that the right-hand one was taken in polarised light.

The photomicrographs are intended only for use as a preliminary elimination for a particular identification. It cannot be overstressed that side-by-side microscopic comparison against freshly made slides of known materials is the only way to achieve a definite isolation.

Two methods have been used in taking the photomicrographs by polarised light: (1) the normal procedure, using a rotating, polarising condenser in the sub-stage holder, and an analyser fitted between the objective and the nose-piece; and (2) by employing two 'polaroid' screens, the apparatus being erected as for normal high-power photomicrography. A Watson 'parachromatic' sub-stage condenser with a focal length of $2\frac{1}{2}$ in. and N.A. 1.0 was used. One of the 'polaroids' was placed between the slide and the sub-stage condenser, and the second in the plane of the eye-piece.

Photomicrographs Nos. 8, 14, 16, 22, 30, 32 and 36 were taken by method (1), and the remainder by method (2).

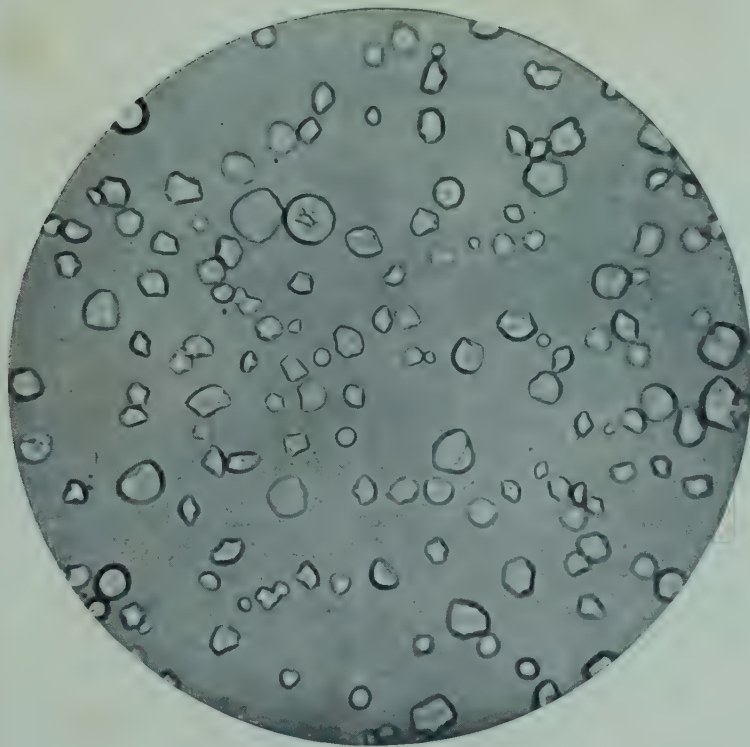
The advantage of the second method was that once a suitable field had been selected for photographing, both the normal and the polarised-light photograph could be more readily taken without losing the field, as it was not necessary to disturb the apparatus in any way. In method (1), however, although the results obtained are probably superior, the difficulty of retaining the same field while the polariser and analyser were interchanged with the normal condenser and objective, was found to be considerable. In addition, with method (1) the illumination at the magnification used was rather too weak to ensure accurate focusing on the camera screen.

The apparatus used for taking the photomicrographs consisted of a Watson 'Bactil' microscope, fitted with a triple nose-piece, a Leitz $\times 10$ 'Periplanatic' eye-piece, and a Watson 'Parachromatic' sub-stage condenser ($F = 2\frac{1}{2}$ in. N.A. 1.0). For the photographs taken at 320 diameters, a Watson $2\frac{1}{2}$ -in. 'Parachromatic' objective (N.A. 0.70) was used, for those taken at higher magnifications a Leitz oil-immersion $1\frac{1}{12}$ in. objective (N.A. 1.32) was substituted. The light-source was a 150 c.p. 'Pointolite' lamp.

The microscope was clamped rigidly in a vertical position on an optical bench. A camera bellows with considerable freedom of extension and fitted to take a $\frac{1}{2}$ plate size ($6\frac{1}{2} \times 4\frac{3}{4}$ in.) photographic plate, was clamped above it. A light-tight connection was made between the bellows and the microscope draw-tube. The 'Pointolite' lamp, fitted in a ventilated lamp-house complete with focusing condenser, was fixed on the optical bench about 18 in. away from the microscope. All the photomicrographs were taken on Ilford special rapid panchromatic plates (backed): 'Backed' plates must be used in order to avoid halation.

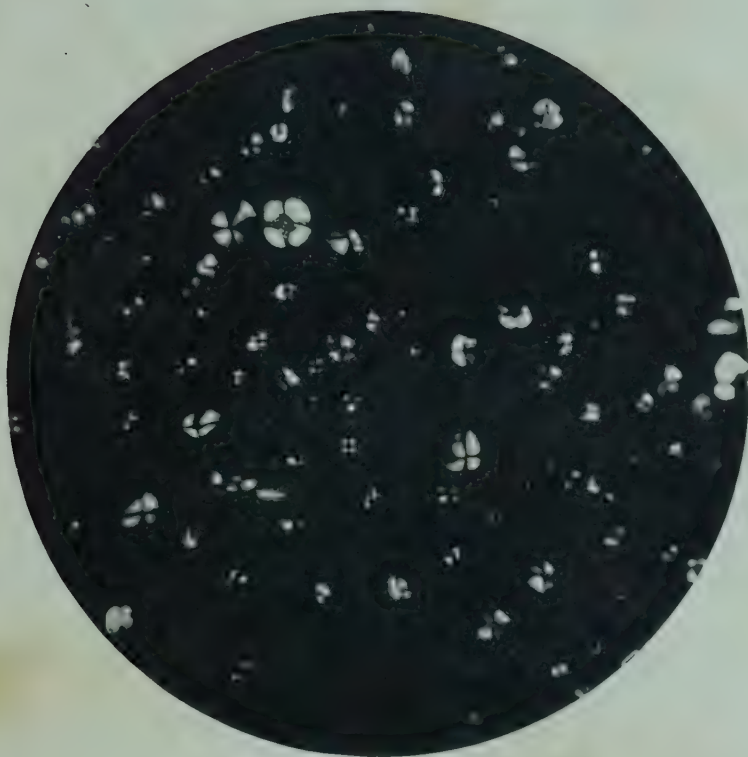
¹ Contributed by E. Young.





Photomicrograph No. 3

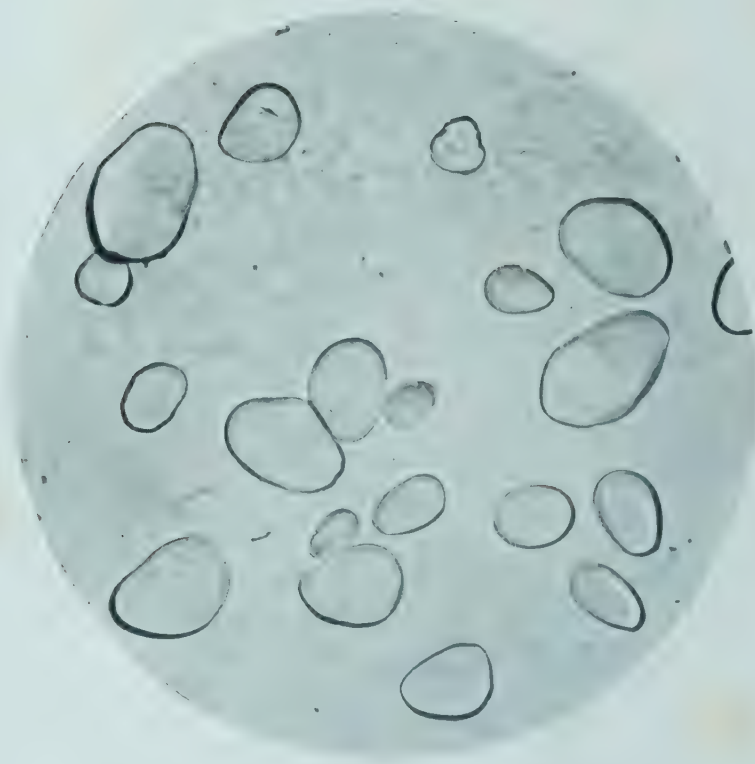
Photomicrographs Nos. 1 and 2 *face p. 320.*



Photomicrograph No. 4.

APIO STARCH.

[Facing p. 444]

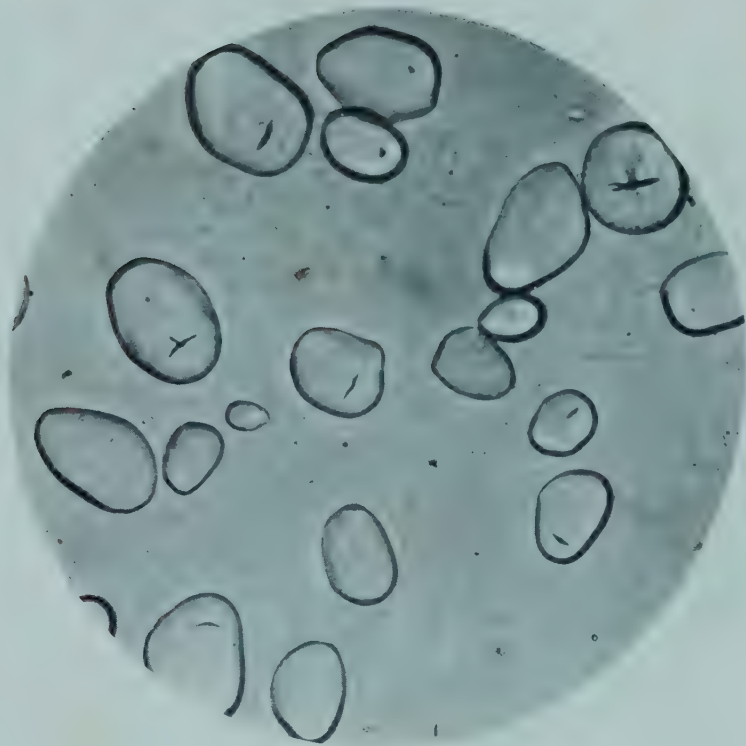


Photomicrograph No. 5.

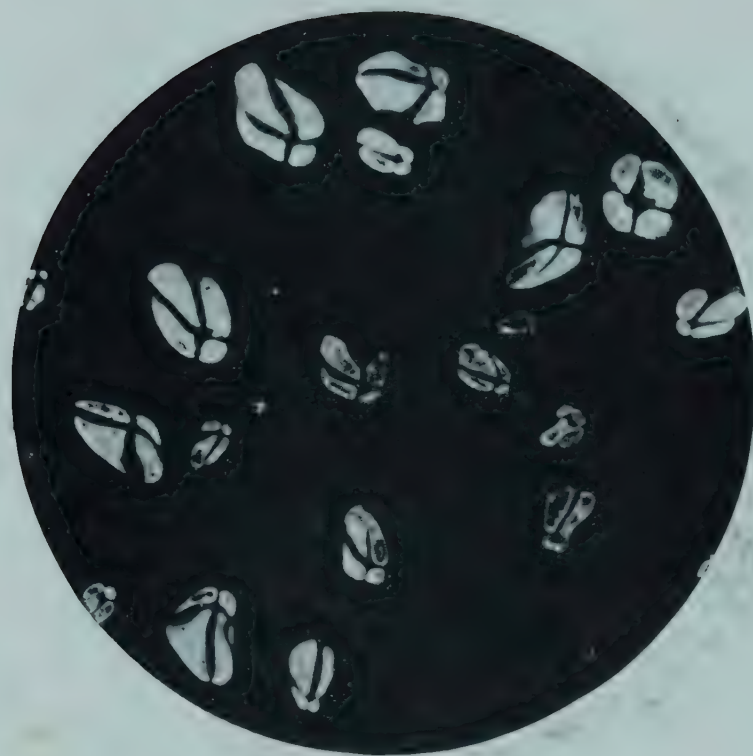


Photomicrograph No. 6.

ARROWROOT STARCH
[*Maranta arundinacea* L.]



Photomicrograph No. 7.



Photomicrograph No. 8.

ST. VINCENT ARROWROOT.

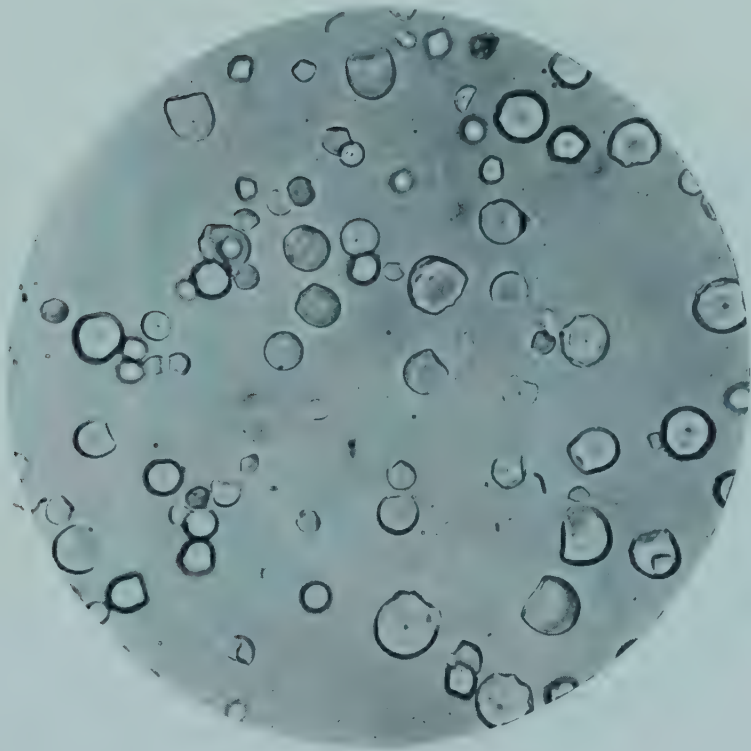


Photomicrograph No. 9.

EDIBLE CANNA STARCH.
[*Canna edulis* Ker.]



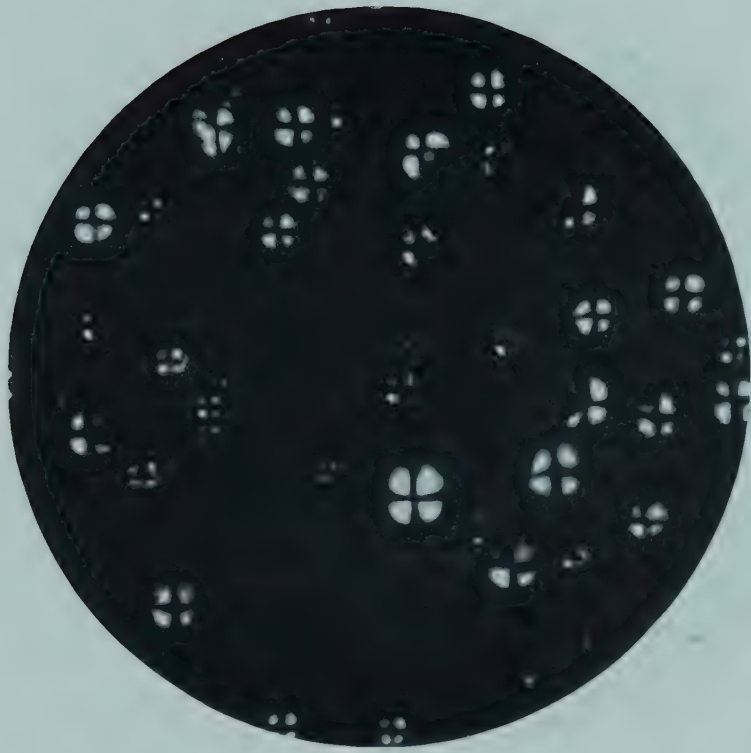
Photomicrograph No. 10.



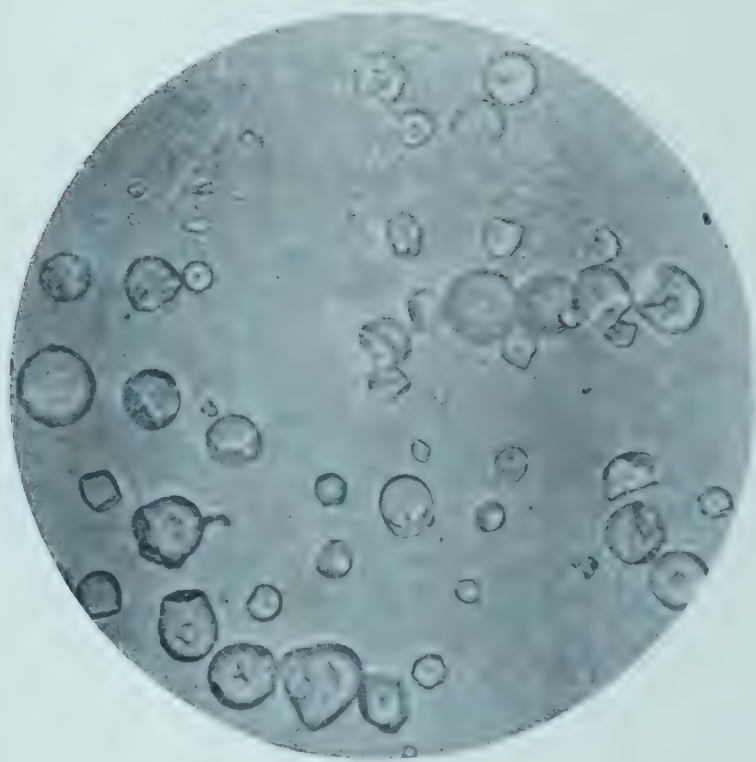
Photomicrograph No. 11.

CASSAVA STARCH.

[*Manihot manihot* (L.) Cockerell.]

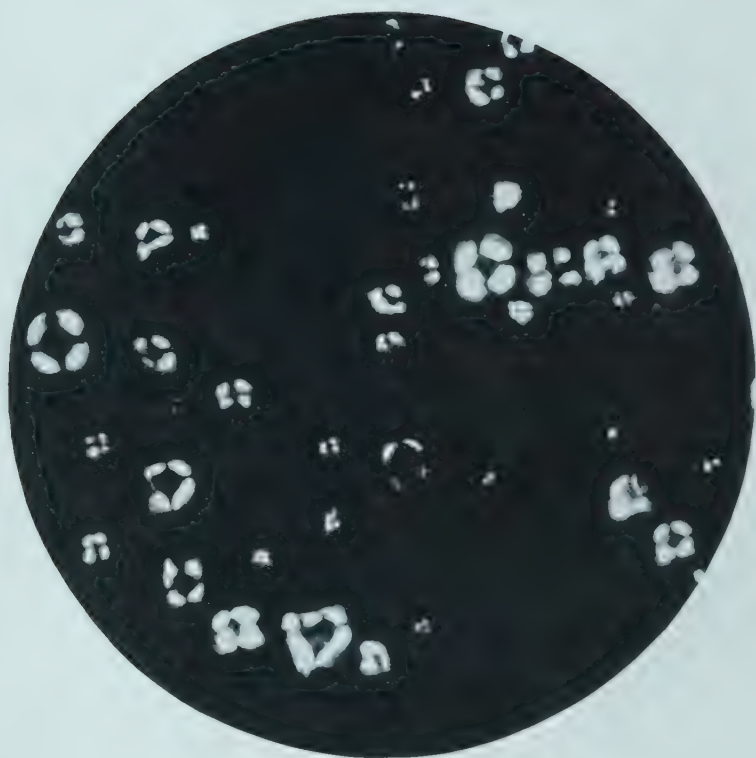


Photomicrograph No. 12.

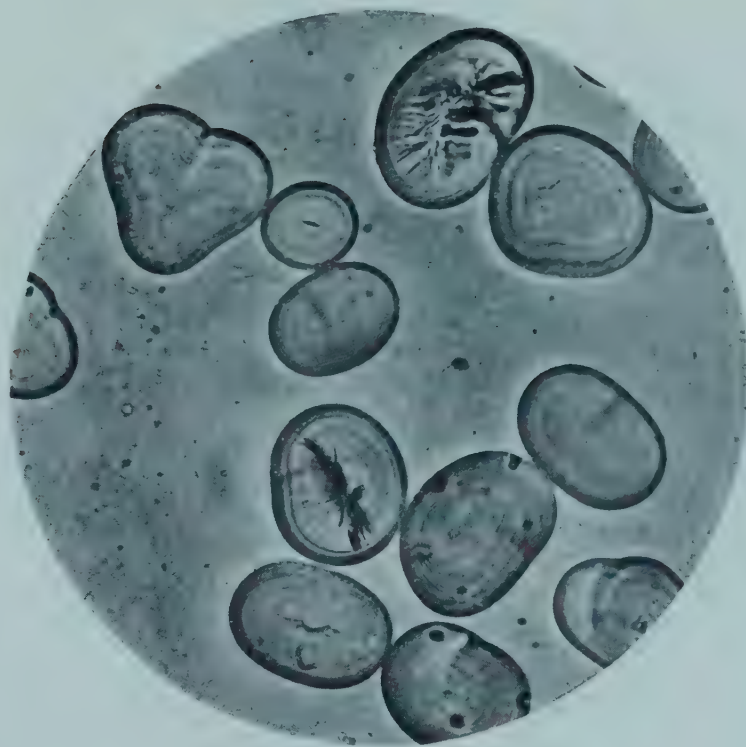


Photomicrograph No. 13.

FARINE DE MANDIOCA.

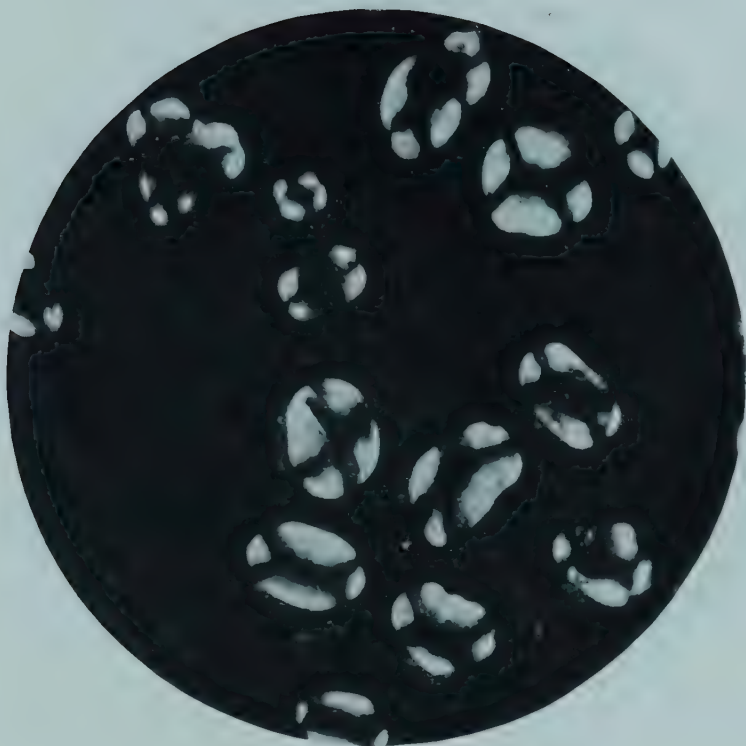


Photomicrograph No. 14.

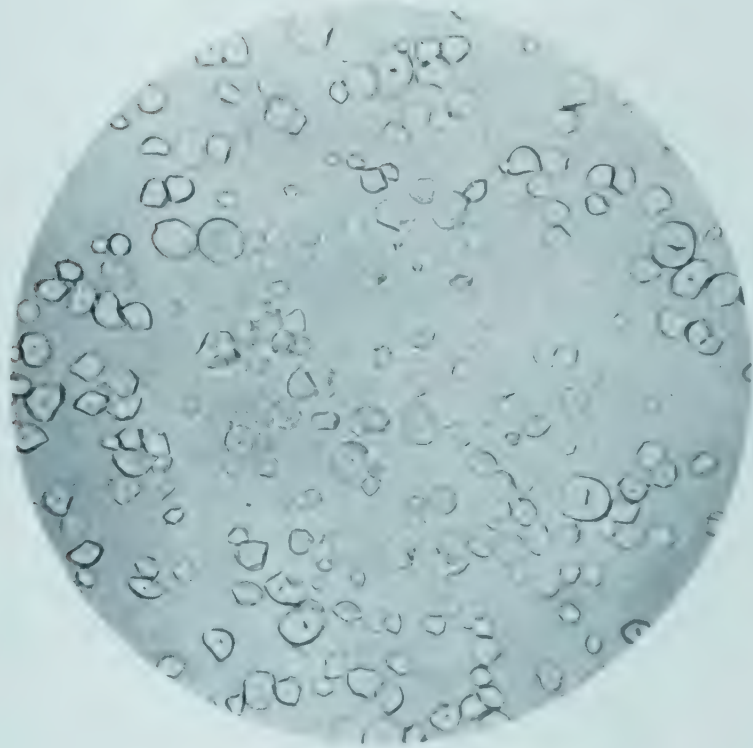


Photomicrograph No. 15.

HARICOT BEAN STARCH.



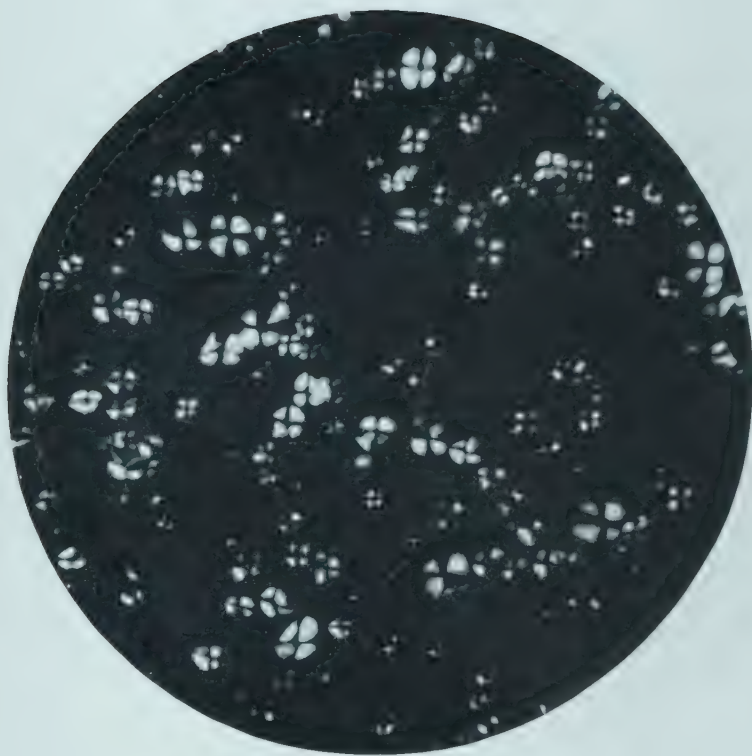
Photomicrograph No. 16.



Photomicrograph No. 17.

NAME HICAMO STARCH.

[*Dioscorea polygonoides* H. and B.]



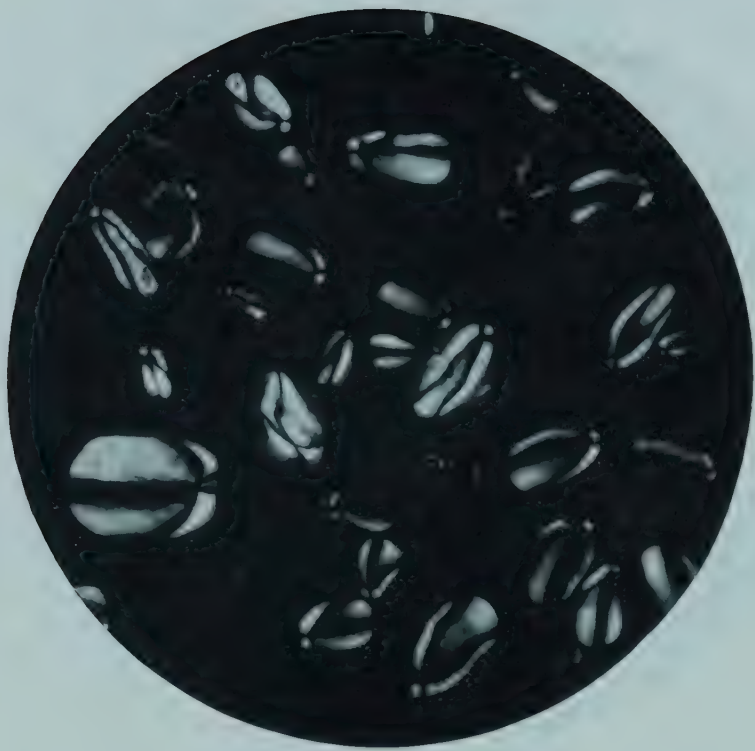
Photomicrograph No. 18.



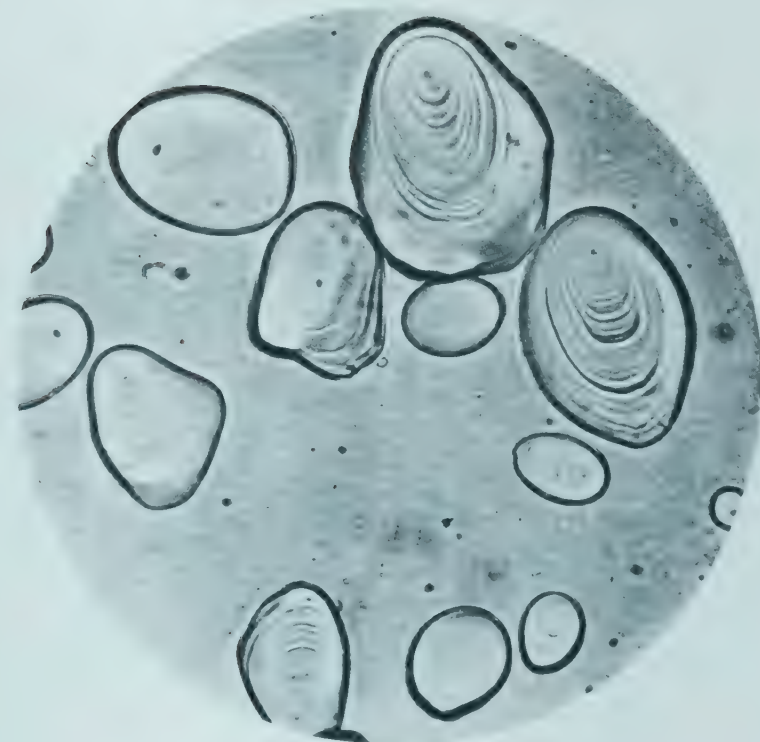
Photomicrograph No. 19.

GREEN PLANTAIN STARCH.

[*Musa paradisiaca* L.]



Photomicrograph No. 20.

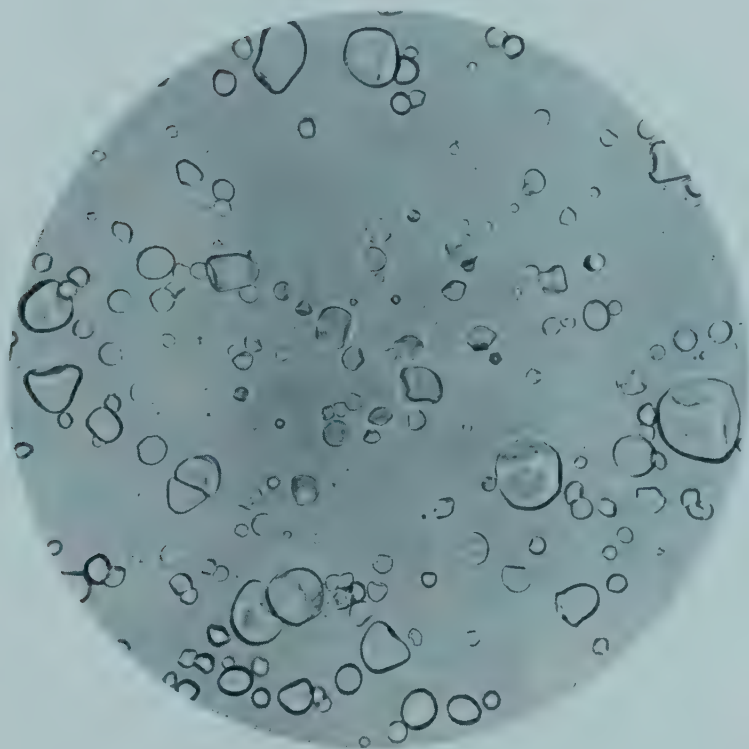


Photomicrograph No. 21.

POTATO STARCH.



Photomicrograph No. 22.



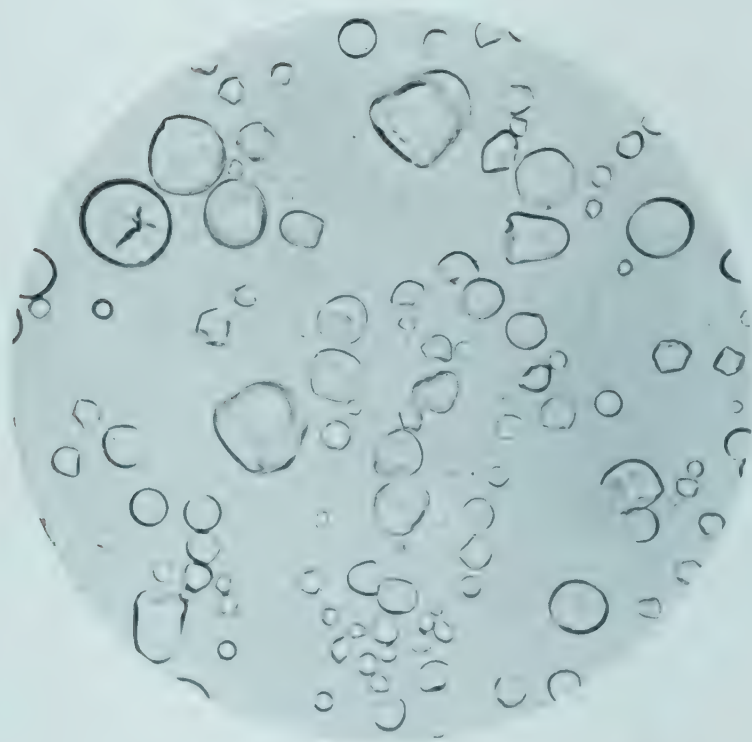
Photomicrograph No. 23.

YELLOW SWEET POTATO STARCH.

[*Ipomoea batatas* (L.) Lam.]



Photomicrograph No. 24.

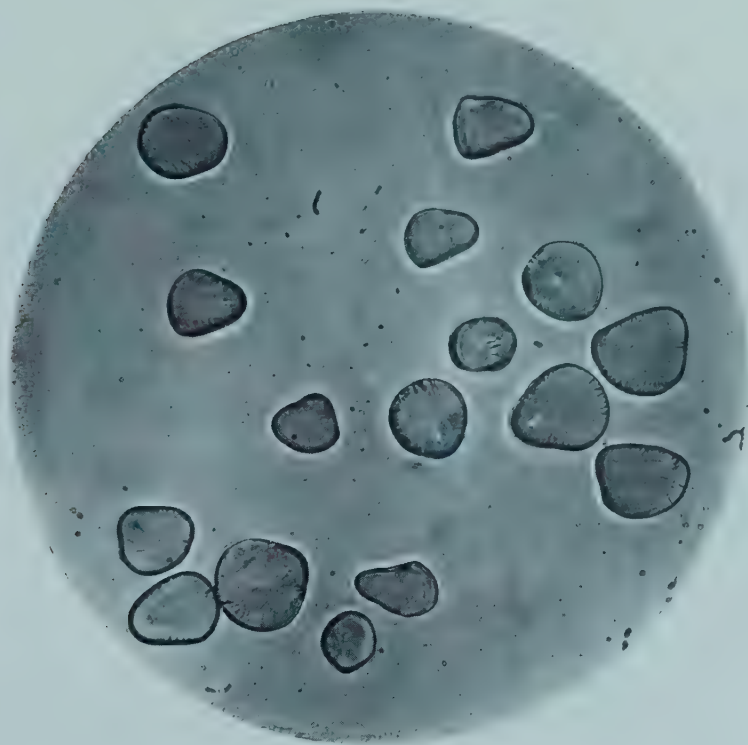


Photomicrograph No. 25.

WHITE SWEET POTATO.
[*Ipomoea batatas* (L.) Lam.]



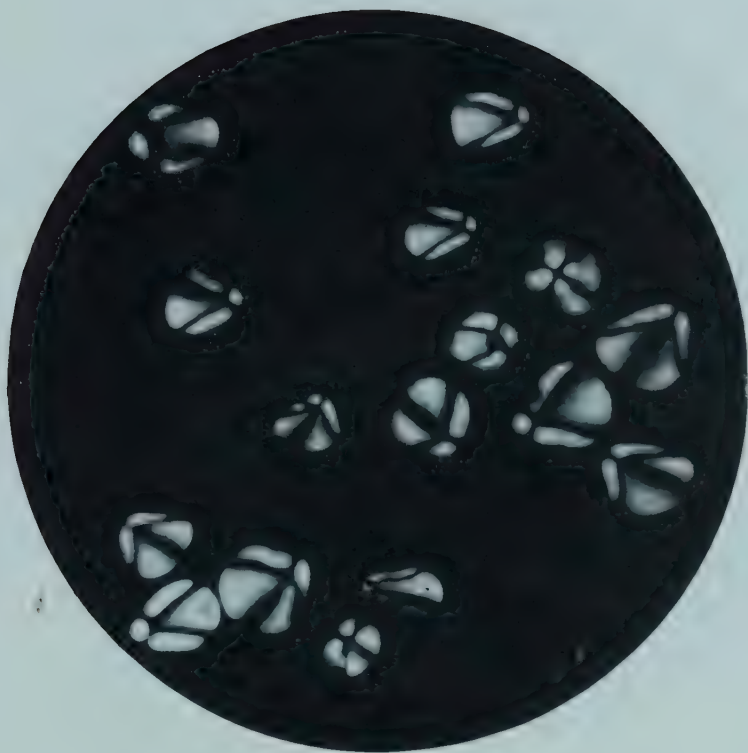
Photomicrograph No. 26.



Photomicrograph No. 27.

LEREN SWEET CORN ROOT STARCH.

[*Colathea allouis* (Aubl.) Tindl.]

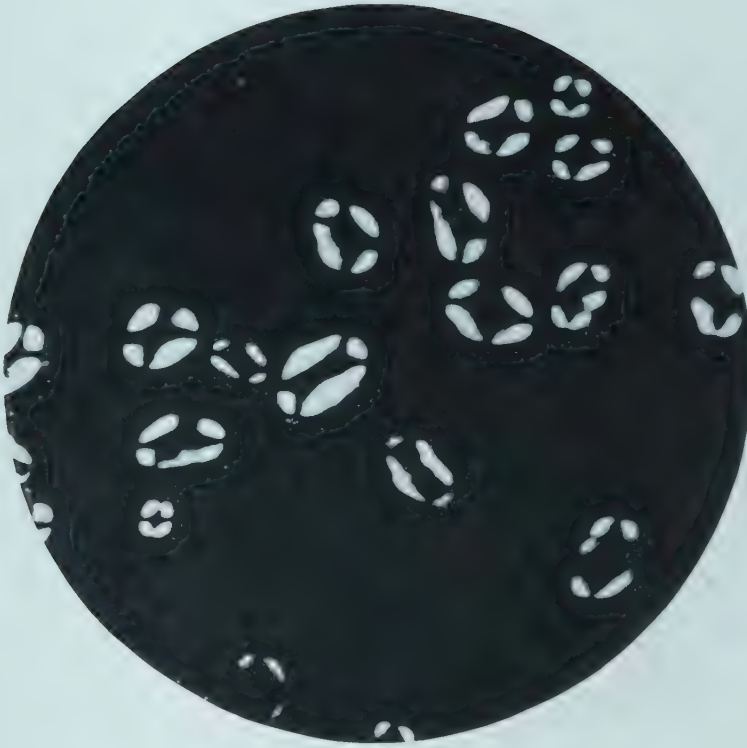


Photomicrograph No. 28.

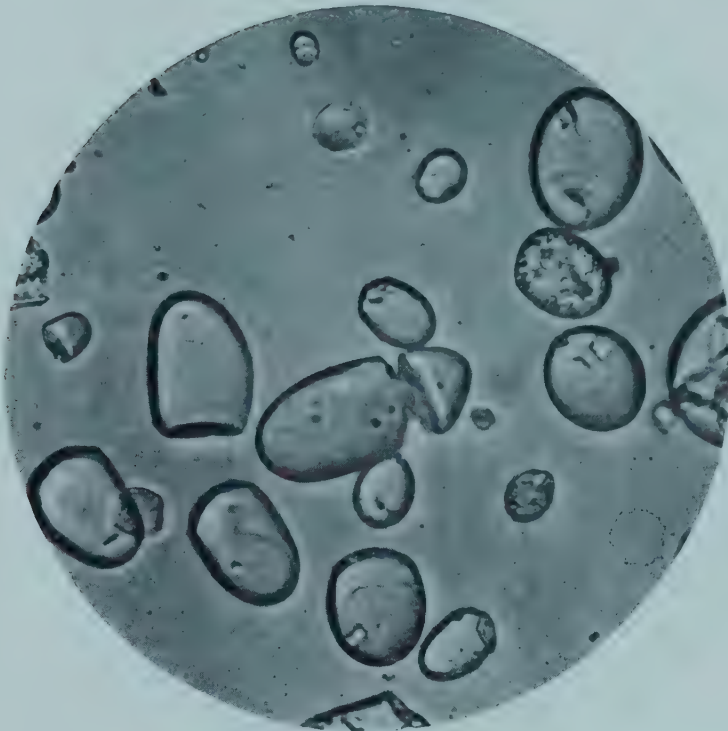


Photomicrograph No. 29.

LENTIL STARCH.
[*Lens esculenta*.]



Photomicrograph No. 30.



Photomicrograph No. 31.

SAGO STARCH.



Photomicrograph No. 32.



Photomicrograph No. 33.

NAME MAPUEY STARCH.
[*Dioscorea trifida* L.f.]

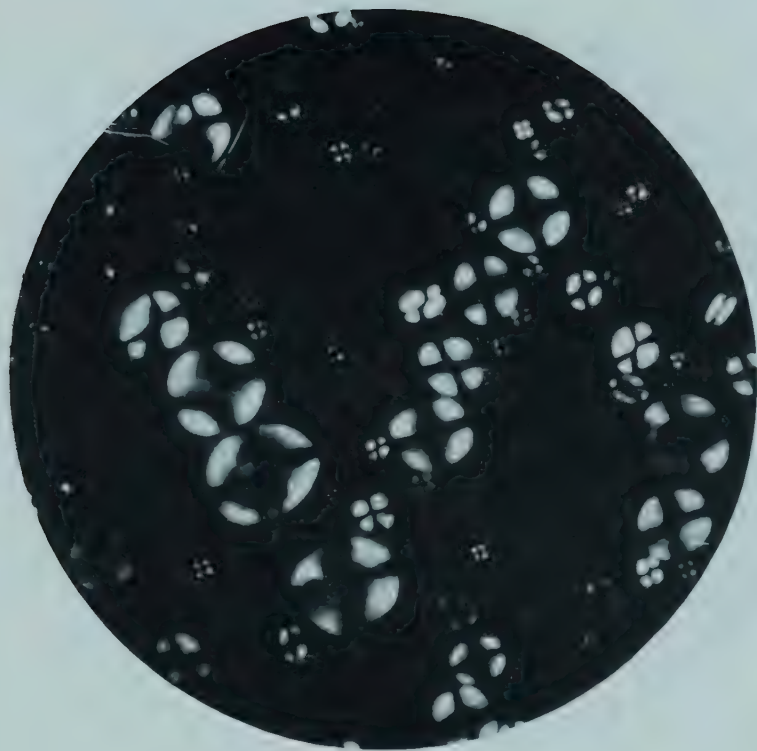


Photomicrograph No. 34.

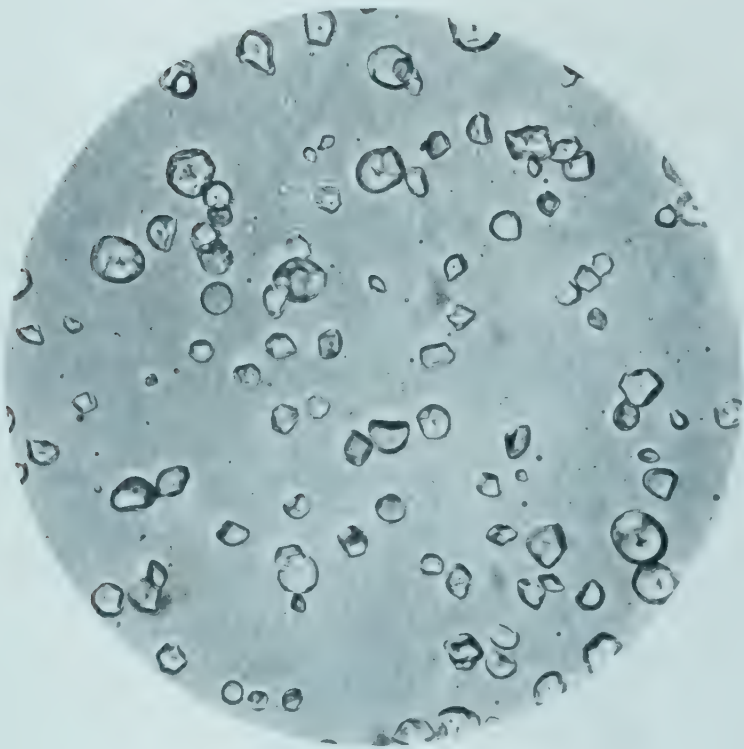


Photomicrograph No. 35.

WHEAT STARCH.



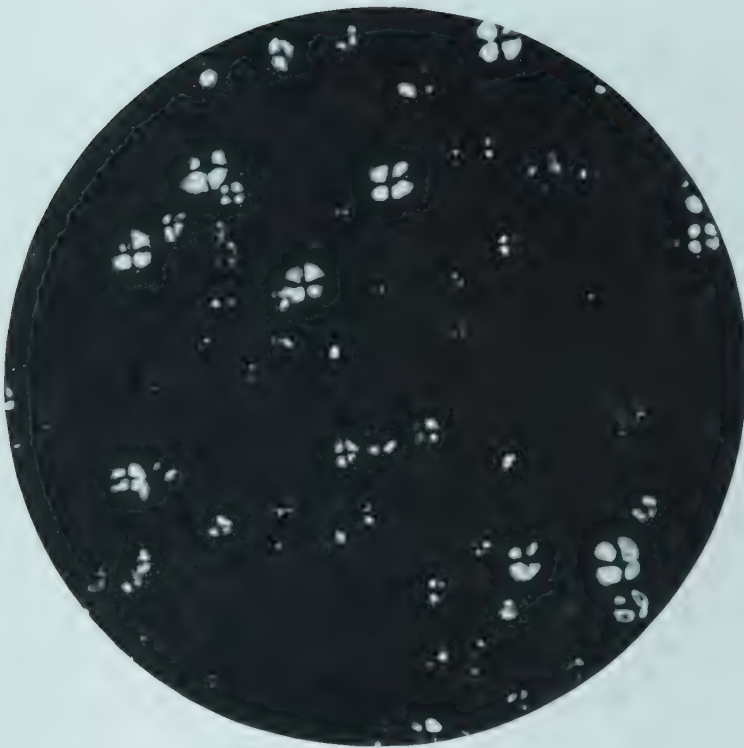
Photomicrograph No. 36.



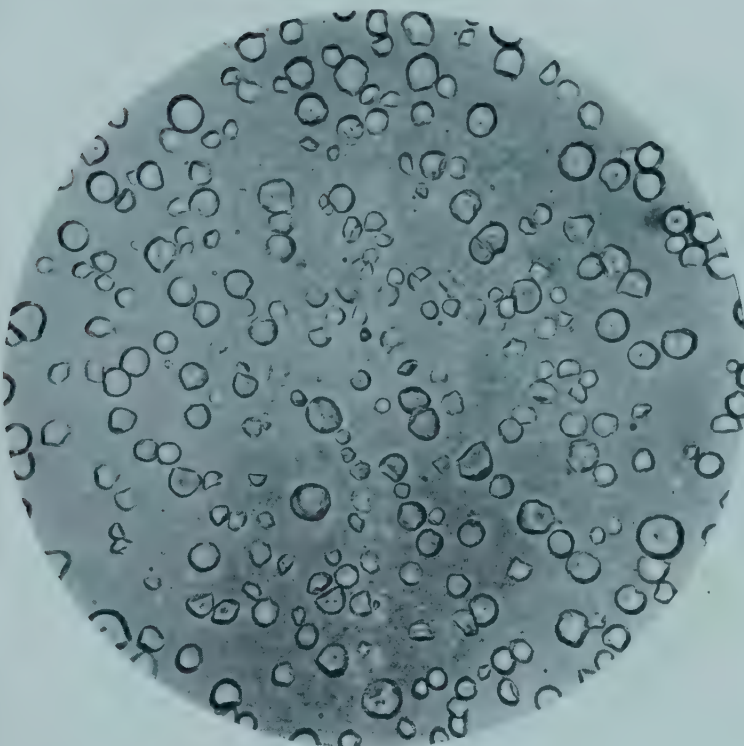
Photomicrograph No. 37.

YELLOW YAUTÍA STARCH.

[*Xanthosoma sagittifolium* (L.) Schott.]



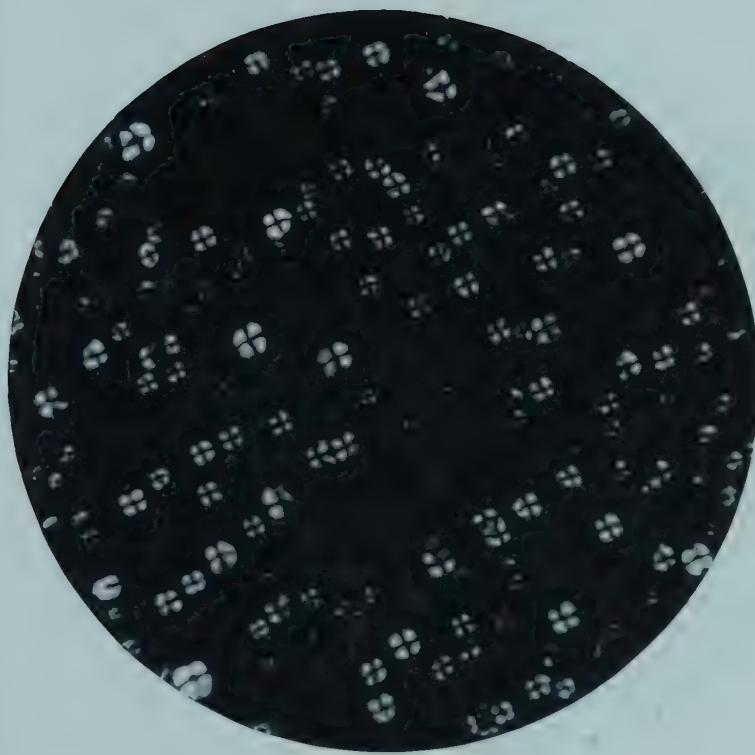
Photomicrograph No. 38.



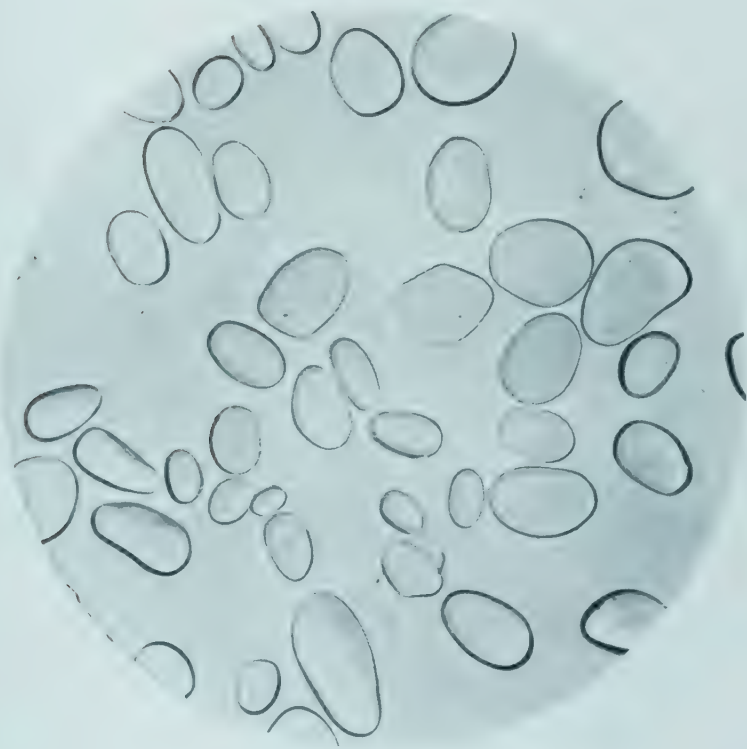
Photomicrograph No. 39.

WHITE YAUTIA STARCH.

[*Xanthosoma caracu* C. Koch and Bouché.]

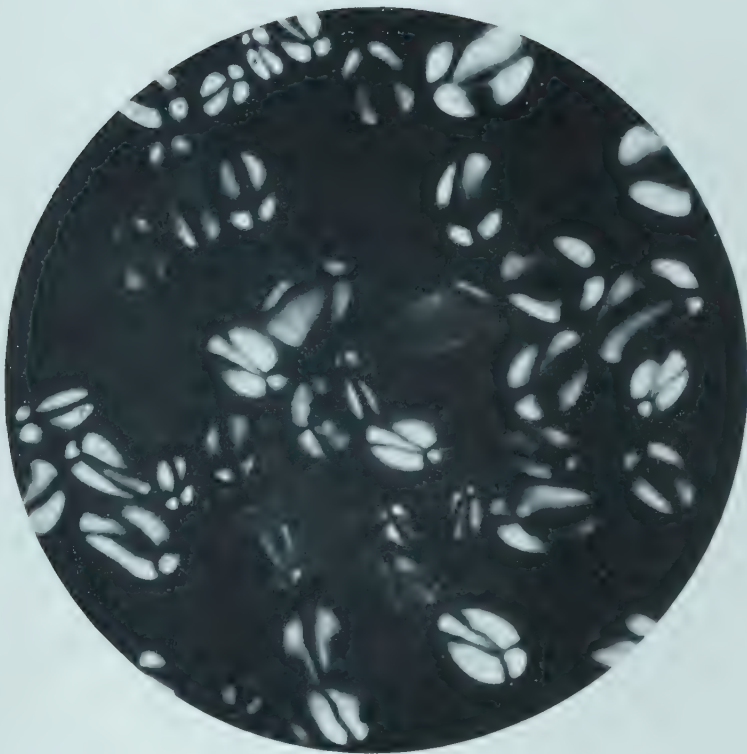


Photomicrograph No. 40.

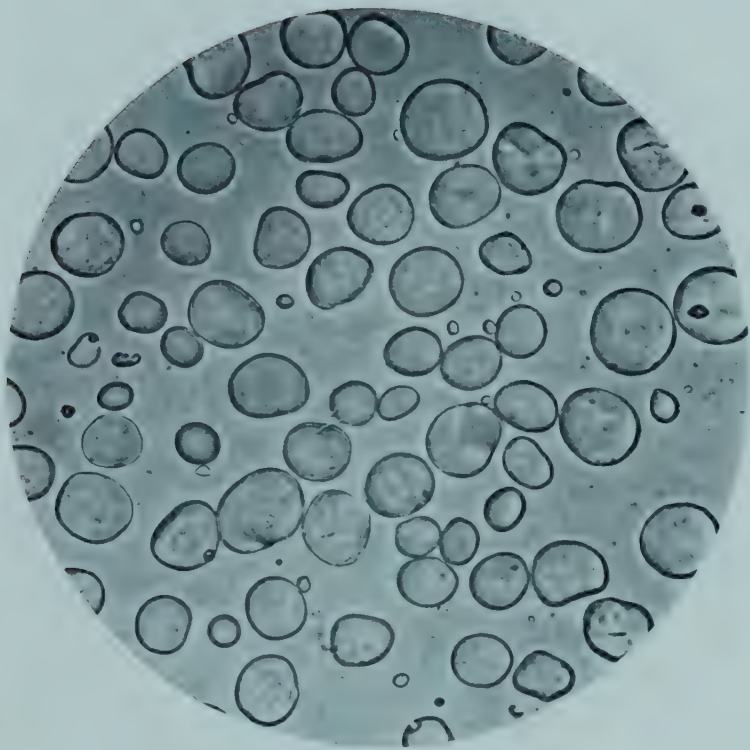


Photomicrograph No. 41.

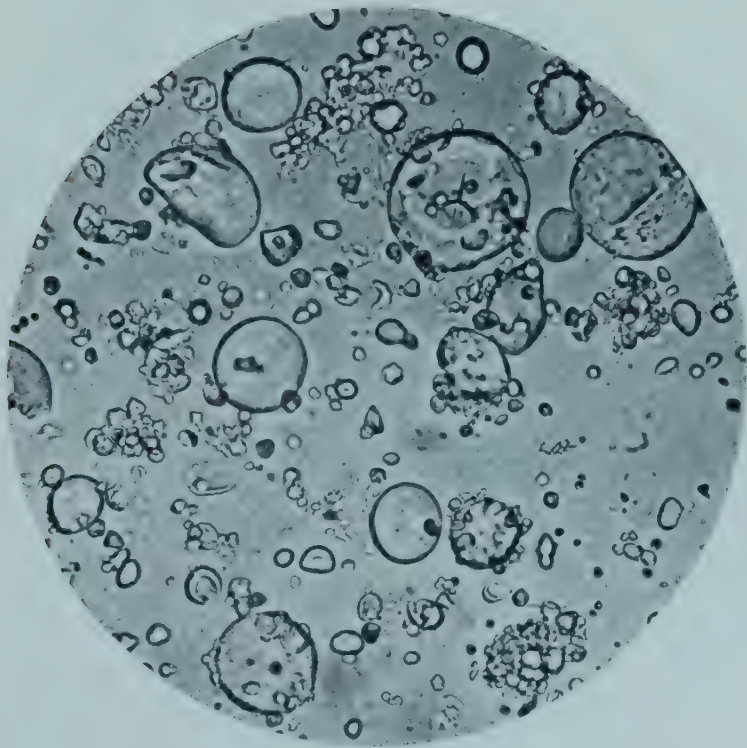
WHITE YAM STARCH,
[*Dioscorea alata* L.]



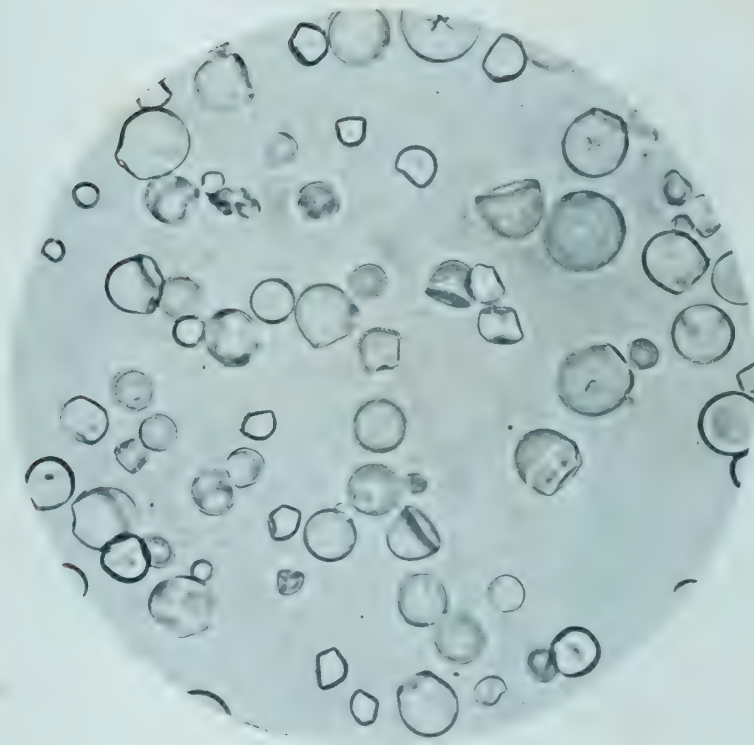
Photomicrograph No. 42.



Photomicrograph No. 44.
BARLEY STARCH.



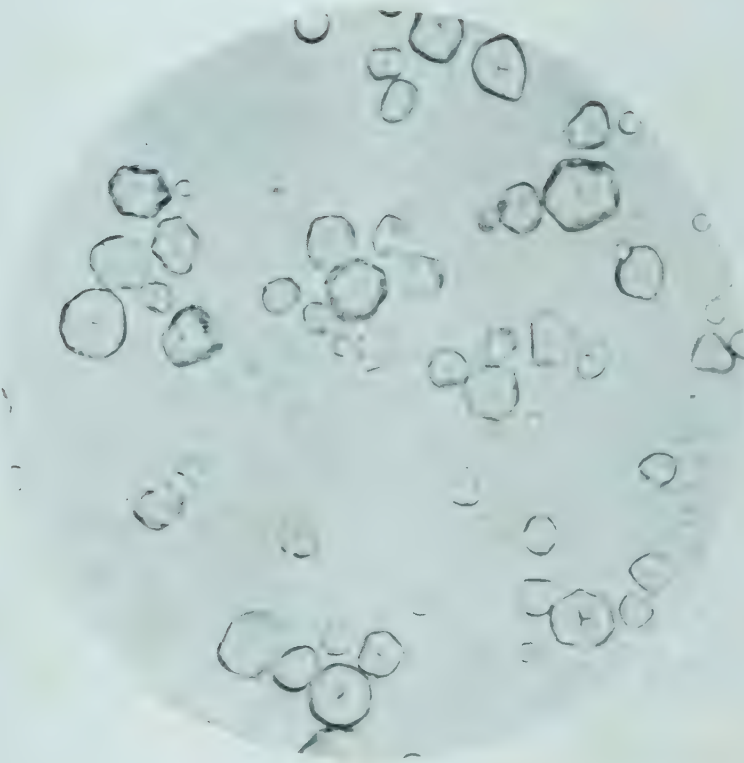
Photomicrograph No. 43.
60 % RYE STARCH.



Photomicrograph No. 45.

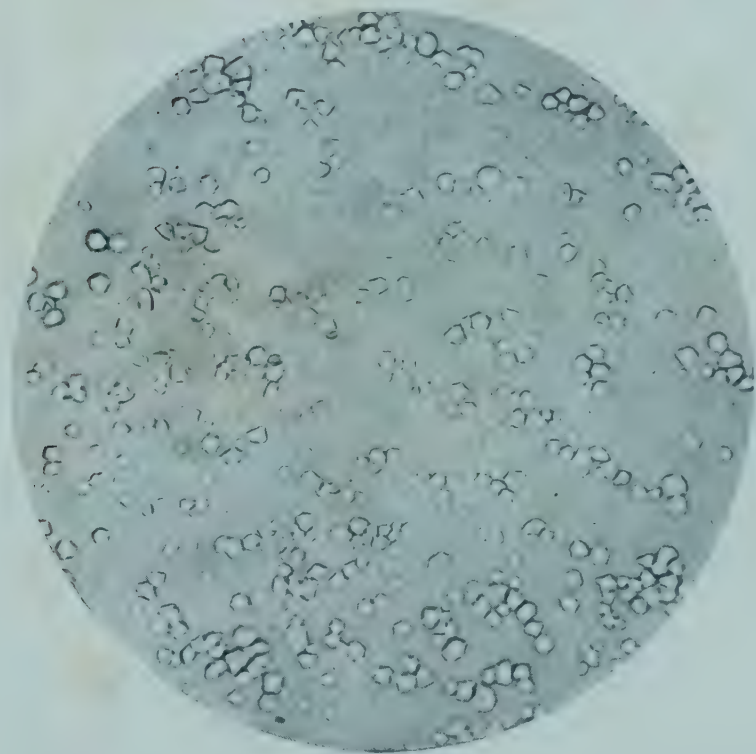
CASSAVA STARCH.

(Cf. Photomicrograph No. 23.)



Photomicrograph No. 46.

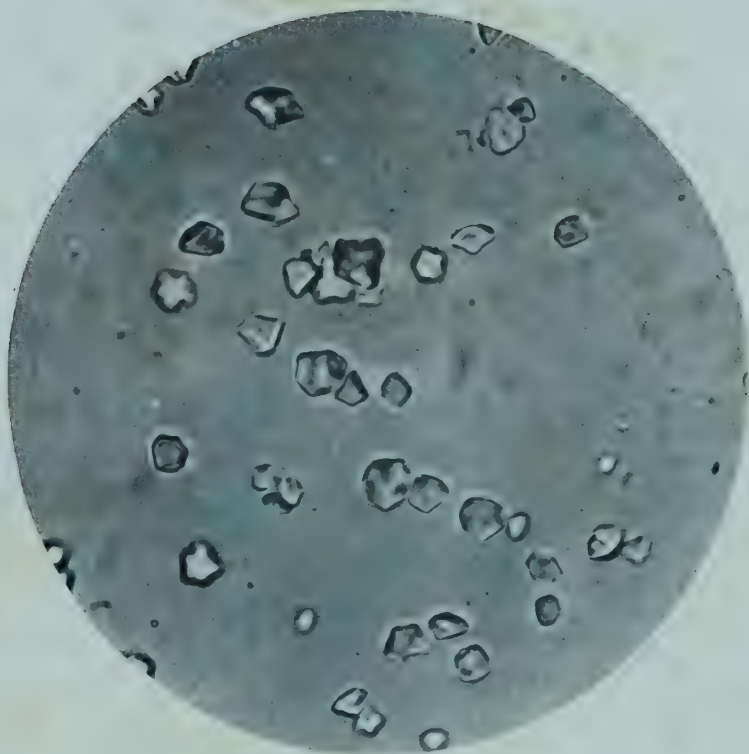
MAIZE STARCH.



Photomicrograph No. 47.

RICE STARCH.

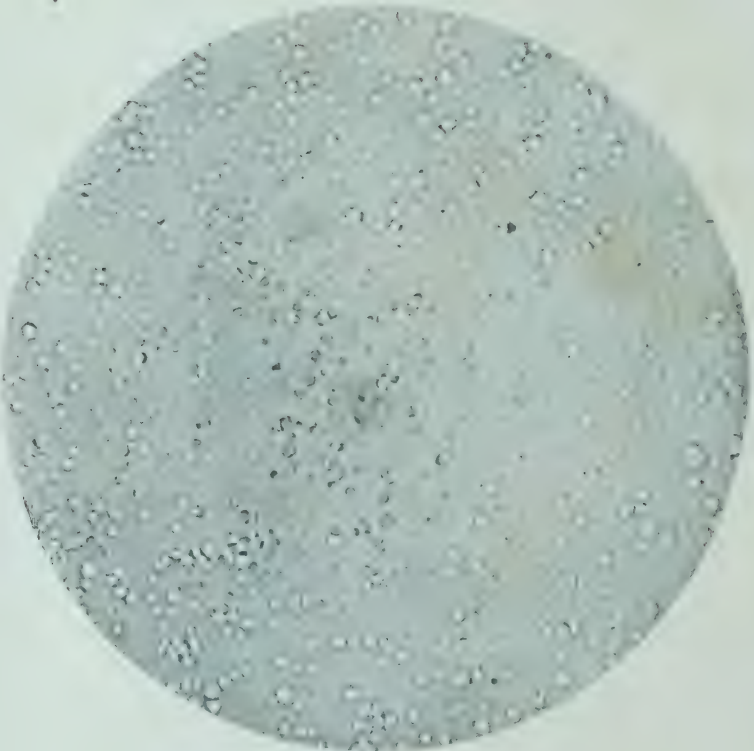
($\times 320$.)



Photomicrograph No. 48.

RICE STARCH.

($\times 640$.)



Photomicrograph No. 49.

TARO STARCH.

[*Caladium colocasia* (L.) W. F. Wight.]

($\times 640$.)

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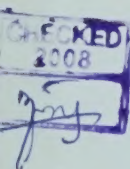
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